Effect of biochar on chemistry, nutrient uptake and fertilizer mobility in sandy soil

by

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DECLARATION

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ABSTRACT

Biochar is a carbon-rich solid material produced during pyrolysis, which is the thermal degradation of biomass under oxygen limited conditions. Biochar can be used as a soil amendment to increase the agronomic productivity of low potential soils. The aim of this study was to investigate the effect of applying locally-produced biochar on the fertility of low-nutrient holding, sandy soil from the Western Cape, and to determine the optimum biochar application level. Furthermore, this study investigates the effect of biochar on the leaching of an inorganic nitrogen fertilizer and a multi-element fertilizer from the sandy soil. The biochar used in this study was produced from pinewood sawmill waste using slow pyrolysis (450 °C). The soil used was a leached, acidic, sandy soil from Brackenfell, Western Cape.

In the first study, the sandy soil mixed with five different levels of biochar (0, 0.05, 0.5, 0.5 and 10.0 % w/w) was chemically characterised. Total carbon and nitrogen, pH, CEC and plant-available nutrients and toxins were determined. The application of biochar resulted in a significant increase in soil pH, exchangeable basic cations, phosphorus and water holding capacity. A wheat pot trial using the biochar-amended soil was carried out for 12 weeks and to maturity (reached at 22 weeks). The trial was conducted with and without the addition of a water-soluble broad spectrum fertilizer. Results showed that biochar improved wheat biomass production when added at low levels. The optimum biochar application level in the wheat pot trial was 0.5 % (approximately 10 t ha^{-1} to a depth of 15 cm) for the fertilized treatments (21 % biomass increase), and 2.5 % (approximately 50 t ha^{-1} to a depth of 15 cm) for unfertilized treatments (29 % biomass increase). Since most biochars are alkaline and have a high C:N ratio, caution should be taken when applying it on poorly buffered sandy soil or without the addition of sufficient nitrogen to prevent nutrient deficiencies.

In the second study, leaching columns packed with sandy soil and biochar (0, 0.5, 2.5 and 10.0 % w/w) were set up to determine the effect of biochar on inorganic nitrogen fertilizer leaching over a period of 6 weeks. It was found that biochar (0.5, 2.5, and 10.0 % w/w) significantly reduced the leaching of ammonium (12, 50 and 86 % respectively) and nitrate (26, 42 and 95 % respectively) fertilizer from the sandy

soil. Moreover, biochar (0.5 %) significantly reduced the leaching of basic cations, phosphorus and certain micronutrients.

This study demonstrated the potential of biochar as an amendment of acidic, sandy soils. Our findings suggest that an application rate of 10 t ha^{-1} should not be exceeded when applying biochar on these soils. Furthermore, biochar application can significantly reduce nutrient leaching in sandy agricultural soils.

OPSOMMING

Biochar is ’n koolstof-ryke, soliede materiaal geproduseer gedurende pirolise, wat die termiese degradasie van biomassa onder suurstof-beperkte omstandighede behels. Biochar kan gebruik word as ’n grondverbeterings middel om die agronomiese produktiwiteit van grond te verhoog. Die doel van hierdie studie was om die effek van plaaslike vervaardigde biochar op die vrugbaarheid van die sanderige grond van die Wes-Kaap te ondersoek, en om die optimale biochar toedieningsvlak te bepaal. Verder, het hierdie studie die effek van biochar op die loging van anorganiese stikstof kunsmis en ‘n multi-elementkunsmis op sanderige grond ondersoek. Die biochar wat in hierdie studie gebruik is, is van dennehout saagmeul afval vervaardig d.m.v. stadige pirolise (450 °C). Die grond wat in hierdie studie gebruik is, is ‘n geloogde, suur, sanderige grond van Brackenfell, Wes-Kaap.

In die eerste studie, is ‘n chemiesie ondersoek van die sanderige grond wat vermeng met is met vyf verskillende vlakke van biochar (0, 0.05, 0.5 en 10.0 % w/w) uitgevoer. Totale koolstof en stikstof, pH, KUK, en plant-beskikbare voedingstowwe en toksiene is in die grondmengsels bepaal. Die toediening van biochar het ‘n veroorsaak dat die grond pH, uitruilbare basiese katione, fosfor en waterhouvermoë beduidend toegeneem het. ‘n Koringpotproef was uitgevoer vir 12 weke en ook tot volwassenheid (wat op 22 weke bereik was) om die effek van die biochar op die sanderige grond teen die vyf verskillende toedieningsvlakke te bepaal. Daar was behandelings met en sonder die bykomstige toediening van ‘n wateroplosbare breë-spektrumkunsmis. Resultate toon dat die toediening van biochar teen lae vlakke koringbiomassa produksie verbeter. Die optimale biochar toedieningsvlak in die koringpotproef is 0.5 % (omtrent 10 t ha^{-1} tot ‘n diepte van 15 cm) vir die bemeste behandeling (21 % biomassa toename), en 2.5 % (omtrent 50 t ha^{-1} na ‘n diepte van 15 cm) vir onbemeste behandelings (29 % biomassa toename). Aangesien die meeste biochars alkalies is en ‘n hoë C:N verhouding besit, moet sorg gedra word wanneer dit op swak-gebufferde of lae N-houdende sanderige gronde toegedien word. Die resultate het aangedui dat die biochar versigtig aangewend moet word om grond oorbekalking te voorkom.

In die tweede studie, was kolomme gepak met 2.0 kg van die sanderige grond gemeng met biochar (0, 0.05, 0.5, 2.5 en 10.0 % w/w) om die effek van biochar op

die loging die anorganiese stikstof kunsmis oor ‘n tydperk van 6 weke om vas te stel. Daar is gevind dat biochar (0.5, 2.5 en 10.0 % w/w) die loging van ammonium (12, 50 en 86 % onderskeidelik) en nitraat (26, 42 en 95 % onderskeidelik) op sanderige grond aansienliek verminder. Verder, het biochar (0.5 %) die loging van basiese katione, fosfor en mikrovoedingstowwe aansienlik verminder.

Hierdie studie het die potensiaal van biochar as verbeteringmiddel van suur, sanderige grond gedemonstreer. Ons bevindinge dui daarop aan dat ‘n toepassing vlak van 10 t ha^{-1} moet nie oorskry word nie wanneer biochar op hierdie gronde toegedien word. Die toediening van biochar op sanderige grond kan die loging van voedingstowwe aansienlik verlaag.

DEDICATION

To Khanyisile and Nokukhanya, may you continue shining bright.

Thank you for always reminding me to stand like a Proper noun.

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CHAPTER 1

1 General Introduction

1.1 Introduction

The threats of nutrient depleted soils associated with food insecurity, global warming and the urgent demand for renewable energy alternatives are a growing global concern. Although several options have been proposed for contending with these issues, no single solution has been found. However, biochar technology has been proposed to offer an integrated approach to contribute to the solution of these challenges (Lehmann and Joseph 2009). The current study draws attention on the effect of biochar applied to a low-nutrient holding acidic, sandy soil.

Biochar is the solid product material produced during a process known as pyrolysis from the thermo-conversion of biomass under little or no oxygen for use in soils as an amendment (Gaskin et al. 2008; Lehmann and Joseph 2009). Biochar is produced from a variety of biomass residues (feedstocks) and under different pyrolytic conditions, and thus has varying nutrient contents. For example, the total nitrogen and phosphorus contents are typically higher in biochars produced from feedstocks of animal origin than those of plant origin (Chan and Xu 2009).

An understanding of the chemical changes that occur in biochar-amended soils is key in managing agricultural soils. This is particularly of importance because the application of biochar to soils as an amendment has shown a number of physico-chemical advantages and disadvantages. For example, several studies have provided encouraging evidence that biochar adds basic cations to soils, improves soil water retention, and has liming potential of acid soils (Glaser et al. 2002; Laird et al. 2010; Sohi et al. 2010; Van Zwieten et al. 2010a). However, although the liming ability of biochar has shown positive responses due to increased biomass production and yields (Lehmann et al. 2003; Rondon et al. 2007; Vaccari et al. 2011; Van Zwieten et al. 2007), negative yield responses have also been found because high soil pH values are often associated with micronutrient deficiencies (Mikan and Abrams 1995).

Although many studies have been conducted on the application of biochar to soils, up until now, no scientific studies have been carried out on South African soils. For

the current study, a sandy, acidic soil was selected as it represents common problematic soils in the Western Cape Province. These soils are typically leached, infertile, with poor nutrient and water holding capacities. Therefore, they meet the requirements for soils that would potentially benefit from biochar amendment. Biochar produced from pinewood sawmill waste produced at 450 °C by slow pyrolysis was chosen as the principal type of biochar as it is readily available on the South African market. Lastly, winter wheat was selected as a model crop as it is widely cultivated in the Western Cape.

1.2 Objectives

The following objectives were investigated on locally produced biochar applied to acidic, sandy Western Cape soil and can be summarized as follows:

1. Investigate the effect on soil chemistry, growth and nutrient uptake of wheat.
2. Elucidate the soil chemical mechanisms behind the positive and/or negative plant growth responses to the addition of biochar.
3. Determine the optimum application level of biochar to the sandy soil to obtain improved soil fertility and maximum plant growth.
4. Determine the potential of biochar to retard or prevent mineral fertilizer leaching.
5. Determine plant available nitrogen remaining in the soil after leaching events.
6. Assess leaching of nutrients from the biochar applied to the soil.

1.3 Thesis structure

The thesis is divided into five chapters: general introduction, a review of the literature, two experimental research chapters, and general conclusion. The chapters contribute to understanding the effect of biochar on soil chemistry, nutrient uptake and fertilizer mobility in soil.

Following a review of the literature on the implications of biochar amendment in soil chemistry in Chapter 2, the first three objectives are addressed in Chapter 3. This chapter is based on the investigation of a wheat pot trial study on nutrient uptake and growth on biochar-amended soil as carried out in two main experiments. In the first experiment, wheat was grown for 12 weeks, and assessed according to the effect of biochar in unfertilized and fertilized treatments. In the second experiment, wheat was

grown to maturity, and assessed based on the effect of biochar in fertilized treatments only. Chapter 4 is divided into two laboratory experiments and addresses the last three objectives through an investigation on the leaching of nutrients from biochar applied to sandy soil. In the first experiment, a six week study investigating the leaching of an inorganic nitrogen fertilizer was performed. In the second experiment, a six week study was carried out to determine the consequence of a multi-element (broad spectrum) fertilizer on biochar-amended soils. Lastly, Chapter 5 gives a brief discussion of the results and draws conclusions from the research. Recommendations and future research are also highlighted.

It is anticipated that the findings from this research will augment the knowledge on the application of biochar to acidic, sandy soil.

CHAPTER 2

2 Literature Review

2.1 Introduction

The widespread problems of an escalating global human population, diminishing food reserves and climate change (carbon abatement) are a growing concern (Lehmann and Joseph 2009). It has been predicted that over the next two decades, crop yields of primary foods such as corn (maize), rice and wheat will considerably decrease as a result of warmer and drier climatic conditions particularly in semi-arid areas (Brown and Funk 2008). In addition to this, agricultural soil degradation and soil infertility are common problems (Chan and Xu 2009; Glover 2009). As a means of addressing these problems, the application of biochar to soils has been brought forward in an effort to sustainably amend low nutrient-holding soils (Laird 2008; Lehmann and Joseph 2009; Yuan et al. 2011b).

Biochar is pyrolyzed (charred) biomass, or also commonly known as charcoal or agrichar, produced by an exothermic process called pyrolysis (Lehmann and Joseph 2009). Pyrolysis is the combustion of organic materials in the presence of little or no oxygen, leading to the formation of carbon-rich char that is highly resistant to decomposition (Thies and Rillig 2009). As a result thereof, biochar can persist in soils and sediments for many centuries (Downie et al. 2011; Glaser 2007; Woods and McCann 1999), and has great potential to improve agronomic production when applied as a soil amendment (Laird et al. 2009).

In previous studies, soils used to investigate the agricultural properties of biochar have mostly been highly weathered soils from humid tropic regions (Glaser et al. 2001; Steiner et al. 2008; Verheijen et al. 2009). Only recently has research included the investigation of biochar application on the performance of infertile, acidic soils with kaolinitic clays, low cation exchange capacity (CEC), and deteriorating soil organic carbon contents (Chan et al. 2007; Chan and Xu 2009; Novak et al. 2009; Van Zwieten et al. 2010b). Generally, the addition of biochar to soil has been reported to have a multitude of agricultural benefits. These include a high soil sorption capacity, reduced nutrient loss by surface and groundwater runoff, and a gradual release of nutrients to the growing plant (Laird 2008).

Furthermore, research on biochar has given evidence that it has potential as a soil conditioner due to its physico-chemical benefits, which include, increased soil water retention and nutrient-use efficiency (Krull et al. 2009; Lehmann et al. 2006), improved soil fertility and enhanced crop production (Glaser et al. 2002). These benefits primarily manifest on account of pyrolyzing dry, fresh biomass to biochar, and thus bring about several gains for nutrient availability. During pyrolysis, labile carbon (C) is converted into a relatively stable aromatised C (Krull et al. 2009), while basic cations are transferred from the fresh biomass to biochar. This is advantageous because when biochar is applied to the soil, these basic cations become available to the soil by occupying the soil exchange sites (Wang et al. 2009).

The scourge of acid soils severely limits plant growth due to aluminium (Al) toxicity and reduced soil fertility. The excessive application of inorganic nitrogen (N) fertilizers rich in ammonium ions (NH_4^+) (Bolan et al. 1991), and anthropogenic activities (Yuan et al. 2011b), can especially add to accelerated soil acidity and consequently depleting soil productivity. Traditionally, lime has been applied to increase soil pH of acid soils with the goal of improved and higher crop yields (Adams 1984). Therefore, since charcoal has been suggested to act as a liming agent (Laird 2008), it is likely that the use of biochar as a soil amendment warrants merit because it can increase soil pH (Van Zwieten et al. 2010b) and aid in decreasing environmental pollution caused by fertilizers (Lehmann 2007a). However, increased pH in biochar-amended soils have been found to cause micronutrient deficiencies, which subsequently result in reduced crop biomass production (Kishimoto and Sugiura 1985; Mikan and Abrams 1995).

On the contrary, a few possible negative implications have been reported to be associated with biochar. Kookana et al. (2011) found that these include i) additional agronomic input costs, ii) the binding and deactivation of synthetic agrochemicals due to an interaction with herbicides and nutrients, iii) the deposit and transport of hazardous contaminants due to the release of toxicants such as heavy metals present in biochar, and iv) an immediate increase in pH and electrical conductivity (EC). Furthermore, although studies have highlighted that contaminants such as organic compounds, heavy metals, and dioxins may be present in biochar, there is

limited published research that proves that these contaminants are available (Smernik 2009; Verheijen et al. 2009).

Owing to the current global growing interest in the application of biochar to soils, a thorough investigation of the potential benefits and negative impacts is warranted. This literature review aims to critically investigate what the causes are for the proposed improvements that the application of biochar to soils has, as well as to highlight some potential negative effects due to biochar amendment. It will examine past and recent research on the effects of biochar on soil amendment by assessing the pyrolysis process, the impact of biochar on soil chemistry, and the effect of biochar on plant nutrient availability. Finally, the coexisting prospective that biochar has regarding mitigating climate change while improving the fertility of soil through carbon sequestration will be discussed.

2.2 Historical background

The dark anthropogenic soils found in Brazil, also known as Amazonian Dark Earths (ADE) refer to black fertile soils called *terra preta de Indio* (Woods and Denevan 2009). These rich black earths are highly fertile and produce large crop yields despite the fact that the surrounding soils are infertile (Renner 2007). Studies involving radiocarbon dating have revealed that these soils were produced up to 7000 years ago during pre-Columbian civilization. It is believed that the accumulation of charcoal in these soils is as a result of anthropogenic activities which consequently led to the formation of *terra preta* soils (Glaser 2007).

Although most dark earths are as a result of long-term human habitation, studies show that chemical changes in the soil are central to the darkening of these soils. These chemical changes encourage soil biotic activity and downward development, and thus resulting in melanization. While these ADE have formed over several millennia, they have not formed at a constant rate. Several studies have found that the rate of formation can fall in the range of 0.015 cm to 1.0 cm per annum. In particular, dark brown to black soils are classified as *terra preta de Indio* based on similarities in texture and subsoil of the underlying and immediately surrounding soil (Woods and McCann 1999).

Dutch soil scientist Wim Sombroek introduced the term *terra mulata* to describe the brown coloured soil which formed as a consequence of semi-intensive cultivation practiced over long periods (Woods and Denevan 2009). Both *terra preta* and *terra mulata* soils are closely associated because they are usually found nearby or embedded within greater regions of each other (Woods and McCann 1999).

Woods and McCann (1999) reported that a distinguishing characteristic between *terra preta* and *terra mulata* is based on what the land is exclusively used for. While *terra preta* originates from human habitation*, terra mulata* is usually found on agricultural land that is used for rigorous agro-forest and crop production. In addition, *terra preta* is darker than *terra mulata* because it exclusively has very high levels of calcium (Ca), potassium (K), and magnesium (Mg) ions. During the decomposition of these basic cations, the soil particulates become better coated than those of the *terra mulata,* and thus give rise to the darker soil colour.

Terra preta has very high concentrations of black carbon that develop from the disposal of charcoal remains from hearths (Glaser et al. 2002), charcoal from cooking and processing fires, as well as settlement refuse burning. In contrast, the lower levels of C found in *terra mulata* are due to *in situ* burning of organic debris (Woods and Denevan 2009). Woods and McCann (1999) suggest that these dark earths did not develop due to shifting cultivation practices or slash and burn techniques, but rather because of slash and char techniques (Chan et al. 2007; Lehmann et al. 2006; Lehmann and Rondon 2006). The former techniques refer to those caused by hot fires that are set at the end of the dry season. These hot fires generate large amounts of carbon dioxide (CO_2) into the atmosphere. Conversely, slash and char techniques have been described as being a form of cool burning due to their low intensity. Their end result is that of an incomplete combustion that has the potential of producing high concentrations of C that can remain in the soil for millennia (Woods and Denevan 2009). The pre-Columbian civilization practiced the slash and char technique by chopping down trees and allowing the remains to smoulder, and thus forming biochar (Renner 2007).

2.3 Pyrolysis process

Traditionally, kilns made from earth, brick or steel were used to produce charcoal. However, these kilns brought about a negative environmental standing because they were related to deforestation and air pollution (Laird et al. 2009). In an effort to combat greenhouse gas emissions, modern day pyrolyzers have been designed to capture these volatiles to produce bio-oil and syngas. The biochar solid product resulting from the biomass pyrolysis process is believed to have merit as it may be useful for renewable energy capture (Sohi et al. 2010).

Today, pyrolysis describes the thermo-chemical process whereby low density biomass (~ 1.5 GJ m^{-3}) and other organic materials are transformed into three useful renewable energy products; viz. bio-oil, biochar, and syngas. This transformation occurs by heating the organic materials to temperatures greater than 400 ˚C in the presence of little or no oxygen. During this process, thermal decomposition of the organic materials occurs and concurrently releases a vapour phase, as well as a remnant solid phase which has come to be known as biochar (Laird et al. 2009).

Of these products, biochar is the principal product of investigation as its importance lies in using it as a soil amendment for both environmental and agronomic advantages, together with a parallel reduction in greenhouse gases (Laird et al. 2009). This highlights the appealing role that biochar, and in particular, pyrolysis, may have in significantly producing bio-energy that may offer environmental solutions towards the supply of green energy (Lehmann and Joseph 2009). However, it has also been found that immediately after pyrolysis, biochar may potentially contain anthropogenic organic contaminants on its surface (Verheijen et al. 2009). These organic compounds may include polyaromatic hydrocarbons (PAHs), and other harmful carbonyl constituents which may show bactericidal and fungicidal activity (Painter 2001). Polyaromatic hydrocarbons are characterized by fused aromatic rings that are commonly found in oil, coal, and tar deposits, as well as the by-products of burning of fossil fuel or biomass. They are alarmingly of concern due to their carcinogenic and mutagenic properties (Kookana et al. 2011).

Pyrolyzing biomass is beneficial for converting unstable C into a more aromatised or stable C (Krull et al. 2009). Therefore, the pyrolyzed biomass has double the carbon

content which is additionally stored in a more persistent form in comparison to ordinary unpyrolyzed (fresh) biomass (Lehmann 2007b).

Literature differs concerning defining actual biochar production temperatures as either high or low-temperature pyrolysis. However, it is generally accepted that depending on the temperature used during the pyrolysis process, either high-temperature (> 500 °C) or low-temperature (< 500 °C) pyrolysis biochars may form. When high temperatures are employed and followed by a series of activation processes, activated carbon, also commonly referred to as biochar, may form. Activated carbon is characterized by high surface areas (>400 m^2 g^{-1}), and a high affinity for the adsorption of metal and organic contaminants (Downie et al. 2009; Johns et al. 1998). High-temperature pyrolysis also produces biochars that are characteristically highly aromatic, and thus recalcitrant to breakdown (Baldock and Smernik 2002). In contrast, when low temperatures are employed, biochar is characterized by a medium to high surface area, and a good affinity for adsorbing organic pollutants from waste water (Lehmann et al. 2006). Also, this biochar yields a greater recovery of C, and other nutrients (feedstock dependent) which are usually lost at higher temperatures (Keiluweit et al. 2010). In practice, low temperature biochars are often employed as they have been shown to have more enhanced soil-biochar interactions relative to high temperature biochars (Joseph et al. 2010). Therefore, biochar is typically produced at a lower pyrolysis temperature and without activation processes (Lehmann 2007b) that would otherwise be used particularly in the production of activated carbon. Consequently, biochar is better to produce than activated carbon given that it requires less energy and cost than activated carbon.

2.3.1 Thermo-chemical technologies

There are four common types of thermo-chemical technologies available for the transformation of biomass into renewable energy products; viz. gasification, flash pyrolysis, slow pyrolysis, and fast pyrolysis. Firstly, gasification is intended to maximize on syngas production. However, its usage requires aerobic conditions, and thus very little biochar and bio-oil are produced from this process. Secondly, flash pyrolysis is intended to maximize on biochar production. As a result thereof, flash pyrolysis gives rise to yields of approximately 60 % biochar and a combined 40 % of bio-oils and syngas. Thirdly, slow pyrolysis gives rise to approximately 35 % biochar,

30 % bio-oil, and 35 % syngas by mass. Lastly, fast pyrolysis has been designed with the intention of maximizing the production of bio-oil; where yields by mass of 50-70 % of bio-oil, 10-30 % biochar, and 15-20 % syngas are produced (Laird et al. 2009).

2.3.2 Different pyrolytic temperatures

High temperature biochar pyrolyzed at 700 ˚C has recalcitrant characteristics and is advantageous when the chief objective is to remove atmospheric CO_2 and sequester C in soil for millennia. However, synchrotron-based near edge X-ray absorption fine structure (NEXAFS) spectra have revealed that biochars produced at high temperatures are typically poorly crystalline (Keiluweit et al. 2010). This implies that some metals in the C lattice may possibly be volatilized, and that the mineral fraction will be less (Bridgwater and Boocock 2006). Therefore, these biochars would consequently have lesser reactivity in soils than lower temperature biochars, which tend to have a better impact on soil fertility (Steinbeiss et al. 2009). It has also been found that biochars produced at temperatures above 700 °C are typically related to the production of PAHs, which are hazardous because of their carcinogenic and mutagenic properties (Garcia-Perez 2008).

In contrast, lower temperature biochar that has been pyrolyzed between 400 and 500 ˚C or under different moisture and pressure conditions has the chief advantage of increasing the soil cation exchange capacity (CEC). Furthermore, this biochar type sequesters soil C, however not to the same extent as high temperature biochar. Instead, the lower temperature biochar will highly benefit the soil fertility characteristics (Antal and Gronli 2003). Garcia-Perez (2008) also found that low temperature biochars pyrolyzed in the temperature range of 350 – 600 °C appear to carry fewer toxic inferences.

A study carried out by Gaskin et al. (2008) showed that biochars produced at 500 ˚C concentrated their most essential plant nutrients; namely P, K, Ca, and Mg. This subsequently led to considerably higher quantities in the final biochar product. Consequently, biochar that is produced with the key role of being a soil fertility amendment needs to be specifically aimed at carbonizing the biomass material under moist conditions and at low temperatures (Novak et al. 2009).

Investigations conducted on the effect of different pyrolytic temperatures on pine chars showed that there was a reduction in the organic content with increasing pyrolytic temperature in the range of 300 to 700 °C. These studies also showed that the weight loss of chars declined from 37 % to 24 % when the biomass was pyrolyzed at 500 °C during different time intervals comprising 10 to 300 minutes. Therefore, it was suggested that pyrolytic temperatures play a more important role than pyrolytic time to carbonize pine wood (Zhou et al. 2009). Other studies revealed that the pyrolysis temperature has an effect on the yield of biofuel and biochar. An increase in temperature resulted in a reduction in the recovery of biochar, while the concentration of carbon increased (Daud et al. 2001; Demirbas 2004).

In a recent study, Cao and Harris (2010) investigated the effect that different heating temperatures have on the physical, chemical, and mineralogical properties of dairy-manure derived biochar. The untreated air dried biochar was dried at a room temperature of 25 °C and used for comparative purposes. Biochar was heated at low temperatures of 100, 200, 350, and 500 °C respectively. It was found that the following properties increased as a result of increased temperature during pyrolysis; specific surface area (SSA), ash content, pH and concentrations of P, Ca, and Mg. The SSA increased exponentially between 200 and 500 °C. The increase in ash content was due to the high presence of calcite and quartz minerals in the manure. At a temperature of 500 °C, the biochar produced more than 95 % ash, thus indicating the complete combustion of C. The pH increase was dependent on the heating temperature. Initially, the untreated manure at room temperature was alkaline at pH 7.5-8.0. At 200 °C, the pH declined to neutrality at about pH 7 (Cao and Harris 2010). This decrease in pH can be attributed to the production of organic acids and phenolic substances which lower the pH as a result of the decomposition of cellulose and hemicellulose (Abe et al. 1998). At temperatures of 300 °C and above, the C began to ash, and subsequently increased the biochar pH to above 10.0, where it became constant (Cao and Harris 2010). In addition, the mean total P, Ca, and Mg concentrations increased from 0.91 %, 3.23 %, and 1.11 %, respectively at 100 °C to 2.66 %, 9.75 %, and 3.02 % at 500 °C. The total P, Ca, and Mg increases were attributed to increasing temperature.

It was generally found that the higher the pyrolysis temperature, the lower the net yield (Cao et al. 2009; Keiluweit et al. 2010). In addition, Cao and Harris (2010) found that a significant decrease in yield was observed at temperatures between 100 and 350 °C. Although the untreated biochar C and N concentrations were high, they decreased with an increase in heating temperature. For instance, the mean C and N were reduced from 36.8 % and 3.12 %, respectively at 100 °C to 1.67 % and 0.04 % at 500 °C due to biomass combustion and organic volatilization. The decrease in NH_4-N was because of N volatilization induced by pyrolysis.

2.3.3 Chemical heterogeneity of biochar

Complex chemical heterogeneity is observed in biochar mainly because of the primary feedstock and pyrolysis process conditions under which it is produced (Lehmann et al. 2011; Schmidt and Noack 2000). Additionally, the presence of heteroatoms, such as hydrogen (H), oxygen (O), N, P, and sulfur (S), incorporated in the aromatic ring also adds to the surface heterogeneity of biochar. This is attributed to the variation in the electronegativity of the heteroatoms relative to the C atoms. A loss of C, H, and O occurs during the pyrolysis process. This loss results in a significant amount of the mineral content initially in the feedstock to be concentrated and passed onto the biochar (Amonette and Joseph 2009). In addition to the chemical complexity of biochar, it has been observed that the volatile matter and fixed C contents give rise to labile and stable compounds of chars respectively (Keiluweit et al. 2010).

2.4 Impact of biochar on soil chemistry

Biochar is becoming a popular alternative to organic amendments that are being applied to soils to increase and sustain soil productivity (Lehmann and Joseph 2009). This is attributed to the large amounts of highly porous black carbon found in biochar. The carboxylate groups found in black carbon provide CEC, increase the O/C ratio, and are the primary source of biochar's high nutrient retention ability (Glaser et al. 2001). In addition, biochar may aid in maintaining or increasing nutrient cycling and the stable pools of soil organic carbon (Gaskin et al. 2008). Despite biochar being able to improve and sustain soil fertility, fresh biochar shows moderately low cation retention properties relative to aged biochar (Lehmann

2007a). Therefore, there is a pertinent area of research required to determine the conditions and time period required for biochar to develop its adsorbing properties.

Leached sandy soils typically have low soil pH values, poor buffering capacities, low CEC, with values ranging from 2-8 $cmol_c\ kg^{-1}$, and can have Al toxicity (Novak et al. 2009). The addition of biochar to highly leached, infertile soils has been shown to give an almost immediate increase in the availability of basic cations (Glaser et al. 2002; Liang et al. 2006), and a significant improvement in crop yields, particularly where nutrient resources are in short supply (Lehmann and Rondon 2006). Over time, these additions continue to promote soil nutrient availability by giving rise to greater stabilization of organic matter and a subsequent reduction in the release of nutrients from organic matter (Glaser et al. 2001; Lehmann and Rondon 2006).

The initial biomass or feedstock used to produce charred biomass is easily accessible because it is usually from the agricultural wastes that farmers would otherwise dispose of. This means that there is a constant supply of agricultural wastes available for producing char (Marris 2006). Sohi et al. (2010) highlighted that using biochar in soil deserves consideration as it assists in improving environmental quality through the control of diffuse pollution and the management of organic wastes. By converting wastes to biochar industry saves on expensive transportation costs (Van Zwieten et al. 2010b). Agricultural wastes are important in soil agro-ecosystems as they are able to provide plant nutrients such as C, N, K, P, Ca, and Mg if they are not disposed of. Above all, when these wastes are used to produce charcoal, they bring about an opportunity to prevent increased fertilizer-use (Laird 2008), and avoid the further reduction of soil organic carbon (Gaskin et al. 2008).

Several studies comparing the application of fresh biomass and biochars of the same biomass into soils with similar soil characteristics have found that primarily due to their recalcitrant nature (Baldock and Smernik 2002; Steiner et al. 2008), biochar, unlike fresh biomass, may persist in soils for hundreds of years (Cheng et al. 2008; Liang et al. 2008; Zimmerman 2010). A long term study involving frequent applications of fresh papermill waste biomass on sandy soil failed to demonstrate the long term build up of soil C (Curnoe et al. 2006). In contrast, Van Zwieten et al. (2010b) found that papermill biochar significantly increased total soil C in the range of 0.5 – 1.0 %. Furthermore, biochar, relative to the fresh biomass of the same

biomass has proven to be effective for carbon sequestration (Vaccari et al. 2011), increasing soil fertility (Wang et al. 2009), and improving the liming potential of acid soils (Yuan et al. 2011b).

A major disadvantage relative to biochar regarding the direct incorporation of fresh biomass to the soil is that because soil fauna are bound to decompose the organic biomass, the fresh biomass will not remain in the soil for long periods of time (Xu et al. 2006). However, since biochar is slow to degrade in the terrestrial environment (Gaskin et al. 2008), it can be used to sequester C in the long-term (Glaser 2007). A key underlying element in the application of charred biomass to soil is that the pyrolysis conditions and feedstock directly affect nutrient availability (Antal and Gronli 2003; Gaskin et al. 2010; Glaser et al. 2002). Therefore, this provides evidence that it is more effective to ameliorate soils with pyrolyzed biomass relative to fresh biomass.

2.4.1 Soil acidity

Soil pH is primarily associated with the monomeric Al hexa-aqua ion [$Al(H_2O)_6$] species on exchange sites. This is due to the influence of the hexa-hydronium species which plays a role in pH buffering. These species undergo quick and reversible hydrolysis reactions which affect solution pH values by releasing or retaining hydrogen ions (H^+). Soil pH has the potential to undergo a change when either the biochar or a cation in the biochar reacts with the soluble monomeric Al species, or alternatively displaces it from the exchange sites of clay or soil organic matter (Sparks 2003).

Depending on the biochar biomass used, basic cations such as Ca, K, Mg, and silicon (Si) can form alkaline oxides or carbonates during the pyrolysis process. Following the release of these oxides into the environment, they can react with the H^+ and monomeric Al species, raise the soil pH, and decrease exchangeable acidity (Novak et al. 2009). Furthermore, research conducted by Novak et al. (2009) on pecan shell derived biochar revealed that there was a high concentration of calcium oxide (CaO) in the biochar, which neutralizes soil acidity as follows:

$$2Al - soil + 3CaO + 3H_2O \rightarrow 3Ca - soil + 2Al(OH)_3 \qquad [1]$$

The reaction describes the reduction in exchangeable acidity whereby Ca replaces the monomeric Al species on the soil exchangeable sites and generates alkalinity. Subsequently, there is an increase in soil solution pH as a result of the reduction of the readily hydrolysable monomeric Al and the subsequent formation of the neutral $[Al(OH)_3]^0$ species (Sparks 2003).

When biochar has high concentrations of carbonates, it may have effective liming properties for overcoming soil acidity (Chan and Xu 2009). In a study conducted by Van Zwieten et al. (2010b), it was shown how the carbonates in the biochar encouraged wheat growth by overcoming the toxic effects of acidic soils.

Both acidic and basic sites may coexist within micrometres of each other on biochar outer surfaces and pore particles. These sites react as both an acid and a base and are known as amphoteric sites. In particular, amphoteric sites are found on oxide surfaces, whose surface charge is dependent on solution pH. Therefore, the surfaces are respectively positively and negatively charged under acidic and alkaline conditions. In contrast, basal surfaces of layer silicates have a permanent negatively charged site in addition to the amphoteric edge sites. Furthermore, carbonate mineral surfaces are analogous to oxide surfaces because of the presence of O in the carbonate anion (Amonette and Joseph 2009).

A corn field study evaluating the effect of the nutrient rich peanut hull biochar on soil nutrients found that soil pH decreased both times during the two growing seasons of investigation in the fertilized treatments. An unspecified nitrogen fertilizer was initially applied at 26 kg ha^{-1}, followed by a side dress application of 166 kg ha^{-1}. At the highest biochar application rate of 22 t ha^{-1}, the soil pH decreased from 6.46 to 5.61 in the 0-15 cm soil depth, and from 6.13 to 5.61 in the 15-30 cm soil depth (Gaskin et al. 2010). This may be attributed to the production of carboxylic functional groups caused by the time dependent oxidation of the biochar surface (Cheng et al. 2006).

2.4.2 Soil carbon

Biochar is synonymous with biomass derived black carbon (Lehmann et al. 2006; Liang et al. 2006), and is consequently commonly referred to as black carbon (BC). Black carbon is a solid residue that forms by the partial burning of plant materials, fossil fuels and other geological deposits**.** The formation of black carbon gives rise to two different products. In the first instance, volatiles re-condense to a soot-BC which is very high in graphite, while the solid residues produce a form of char-BC. Black carbon generally encompasses C forms of varying aromaticity and falls along a broad spectrum that includes charred organic materials to charcoal, soot and graphite (Schmidt and Noack 2000).

Black carbon is highly resilient given that it is able to persist in the environment for hundreds and thousands of years. This characteristic is established in the black carbon's inherent nature of being chemically and microbially stable because of its polycyclic aromatic structure. The oxidation of BC causes a continual production of carboxylic groups on the edges of the aromatic backbone and a resultant increase in its nutrient holding capacity (Glaser et al. 2001).

Biochar is primarily composed of both single and condensed ring aromatic C, and subsequently has a mutual high surface area per unit mass and a high surface charge density (Lehmann 2007a). The biochars largely composed of single-ring aromatic and aliphatic C mineralize more rapidly in comparison to those composed of condensed aromatic C (Lehmann 2007a; Novotny et al. 2007). Spectra using NEXAFS reveal that aromatic and quinonic compounds are more common when aliphatic groups are lost at 400 ˚C (Keiluweit et al. 2010).

Lehmann (2007a) reported that biochar may be an alternative to renewable energy because it is not carbon neutral, but rather carbon negative. This implies that because biochar is formed by a carbon negative process, it may serve as a long-term terrestrial sink of carbon. The carbon negative process means that the feedstock parent material used to manufacture biochar initially withdraws organic carbon from the photosynthesis and decomposition carbon cycle pathways (Lehmann 2007b). This process is then followed by storing this organic carbon in the soil, thus causing it to accumulate over time (Glaser 2007). Relative to merely using

fresh material to store C, because biochar decomposes over a long period of time, it is able to create the slow release of CO_2 into the atmosphere over an extended period, and thus reduce CO_2 emissions (Gaunt and Lehmann 2008). Therefore, because biochar is able to gain CO_2 from the atmosphere, it would circumvent from the contribution of climate change, and hence aid in reducing global warming (Lehmann 2007a).

Ideal carbon sequestration involves no negative soil effects as a result of the additional carbon input. In the case of using biochar, this means that the crop quality and yield, would be enhanced, with no incidence of harmful pests and crop diseases (Vaccari et al. 2011). Busscher et al. (2010) proposed that using non-activated pecan shell derived biochar to increase soil C would improve soil physical properties. Switchgrass (*Panicum virgatum)* was added for this purpose. It was found that although switchgrass increased soil C, it is likely that the results will be transitory due to the rapid oxidation rate of the soils and climate.

2.4.3 Effect on pesticides (biocides)

Biochar has proven to be valuable in being an adsorbent for both nutrients and organic contaminants (Laird et al. 2009), and it further has the potential to play a role in the sorption of pesticides in soils (Sheng et al. 2005). It has been suggested that the pesticide sorption in soils was altogether a property of both easily oxidized soil organic matter and chars that are resistant to hydrogen peroxide due to the burning of sugarcane wastes (Sheng et al. 2005). However, a potential problem that has been observed is that the addition of a small quantity of biochar to soil is able to inhibit the microbial degradation of pesticides, and thus improve their persistence in the environment (Yu et al. 2009).

Chars are normally regarded as super sorbents for hydrophobic organic compounds (HOCs), and thus have an effect on the environmental fate and bioavailability of HOCs (Zhou et al. 2009). The sorption of benzene to biochar has been found to show a very strong ability to possess markedly dissimilar sorption and desorption isotherms, particularly at low benzene concentrations. This property is known as hysteresis (Smernik 2009).

Yu et al. (2009) investigated the effect of red gum wood biochars, produced between 450 and 850 °C and applied between 0 and 1 % by weight, on the plant bio-availability and uptake of pesticide residues by spring onion (*Allium cepa*) when incorporated in red brown sandy loam soil. The results indicated that the biochar produced at 850 °C was more effective than the former because of its greater surface area, nanoporosity, decay rate, and capacity to sequester organic compounds. Carbofuran and chloropyrifos are common insecticides that were used for the study. It was observed that the concentrations of these insecticide residues decreased with time as leaching from the soil was not allowed. This was attributed to dissipation (degradation and/or sequestration) associated with an increase in the biochar application level.

The effect of biochar on organic pollutants has been proven to have various influences on the chemical properties of the soil. A great advantage is the reduction in the bioavailability, toxicity, and mobility of organic pollutants in contaminated soils. In contrast, the application of biochar to these soils has the disadvantage of decreasing the efficiency of pesticides and herbicides applied to the soil. As the biochar ages, the soil develops a limited sorption capability of these pesticides and herbicides, and thus resulting in its sorption ability being ineffective over time (Smernik 2009).

Investigations conducted on the effect of different pyrolytic temperatures on wheat straw established that charcoals produced at high temperatures between 500 and 700°C predominantly contained carbonized carbon over organic carbon. This meant that the uptake of benzene and nitrobenzene was surface adsorbed. In converse, charcoals produced at temperatures below 500°C mainly contained organic carbon. This led to the incomplete carbonization of benzene and nitrobenzene, and thus resulted in the compounds being absorbed as partition medium (Zhou et al. 2009).

2.4.4 Effect on plant growth

Numerous and regular applications of biochar to soil are not necessary because biochar is not warranted as a fertilizer (Lehmann and Joseph 2009). In a pot trial carried out by Chan et al. (2007), a significant increase in the dry matter (DM) production of radish resulted when N fertilizer was used together with biochar. The

results showed that in the presence of N fertilizer, there was a 95 to 266 % variation in yield for soils with no biochar additions, in comparison to those with the highest rate of 100 t ha^{-1}. Improved fertilizer-use efficiency, referring to crops giving rise to higher yields per unit of fertilizer applied (Chan and Xu 2009), was thus shown as a major positive attribute of the application of biochar.

Major et al. (2010) conducted a study whereby a field trial demonstrated that a single dolomitic lime and wood biochar application on an acidic, infertile Oxisol was sufficient to increase crop yield and nutrition uptake of crops. A maize-soybean rotation was used for the study which took place over several cropping seasons. In addition, inorganic fertilizers were equally applied to both the biochar-amended and control soils. The trial was carried over 4 years. It was found that no significant effect was observable during the first year of application. However, the maize yield gradually increased with an increase in the biochar application rate in the ensuing years. These yield increases were as a result of increases in pH and nutrient retention. It was found that there was a stark overall decline in yield in the fourth year of application due to the decreasing Ca and Mg soil stocks.

2.5 The effect of biochar on plant nutrients and non-essential elements availability

Plant nutrient uptake and availability of elements such as P, K and Ca are typically increased, while free Al in solution is decreased in solution in biochar-amended soils. This occurs as a function of biochar's high porosity and surface to volume ratio, together with an increase the in the pH of acid soils, attributed to the basic compounds found in biochar (Chan et al. 2007).

When comparing pyrogenic organic material such as biochar to ordinary organic matter, it was found that the chief distinguishing characteristic between the two products is that biochar has a much higher sorption affinity and ability for sorbing non polar organic compounds. These compounds refer to polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), herbicides, and pesticides. Furthermore, the pyrogenic organic material showed signs of being less reversible than other forms of organic matter, and of displaying non linear sorption isotherms. This is indicative of adsorption onto biochar surfaces. This ability for sorption is essential in

controlling the fate and behaviour of organic and environmental pollutants (Smernik 2009).

Liang et al. (2006) reported that both an increase in surface oxidation and CEC are the possible reasons for the long term effects that biochar has on nutrient availability. Various studies continue to prove that the increase in soil fertility of ADE is attributed to charcoal. Lima et al. (2002) showed that P and Ca accumulated from bone apatite due to anthropogenic activities, while black carbon arose from charcoal (Glaser et al. 2001).

2.5.1 Macronutrients

Nitrogen

Plant based biochar consists of various N containing structures which include amino acids, amines, and amino sugars. When subjected to pyrolysis, these structures get condensed and form heterocyclic N aromatic structures (Cao and Harris 2010; Koutcheiko et al. 2006), which may possibly not be available for plant use (Gaskin et al. 2010). Consequently, the residual N in the biochar is largely found as recalcitrant heterocyclic N rather than bio-available amine N (Cao and Harris 2010; Novak et al. 2009). For agronomic purposes, and to counter the potentially unavailable biochar N it has been found that there is a positive effect when biochar was applied together with the addition of a N fertilizer (Chan et al. 2007; Steiner et al. 2008), thus showing that biochar has the potential to improve the efficiency of mineral N fertilizer. In addition, biochar is suggested as being economically viable due the reduction in the amount spent on commercial mineral fertilizers (Steiner et al. 2008).

Although not fully understood, empirical research has shown that biochar alters the N dynamics in soil (Lehmann 2007a). Weathering of biochar in soil has been shown to lead to N immobilization (Singh et al. 2010) primarily attributed to high C contents of leaching sources (Laird et al. 2010; Lehmann et al. 2003). Also, depending on biochar feedstock, soil and contact time period, high biochar application levels between 10 and 20 % by weight have been shown to reduce NH_4^+ leaching in contrasting (Ferralsol and Anthrosol) soils (Lehmann et al. 2003). Furthermore, Chan et al. (2007) observed an increase in the uptake of N at higher levels of biochar. Since nitrogen is primarily assimilated by plants as nitrate (NO_3^-), it is imperative that

its uptake be coupled with an uptake of basic cations in order to maintain electrical balance. Consequently, this is associated with a considerable increase in K uptake, and a slight Ca uptake.

The determination of soluble NH_4-N is typically used to assess the potential of a material to be used as a soil amendment. Consequently, in a study conducted by Cao and Harris (2010), it was determined that it was better to carbonize the dairy manure derived biochar at a low temperature of less than 200°C, than at higher temperatures. This was done to ensure that the NH_4-N content of the biochar was favourably used as an effective soil amendment for the nutrition of the crop.

Common N functional groups for low temperature biochar were measured by X-ray photoelectron spectroscopy (XPS) and found to be pyrrolic or pyridinic amines (Amonette and Joseph 2009). Nitrate nitrogen (NO_3-N) and ammonium-N are mineral forms of N, and are found in low concentrations in biochar. However, the availability and rate of mineralization of organic N found in biochar applied to soil provides an indication of the biochar's ability of being a slow release N fertilizer (Chan and Xu 2009).

In a study carried out using pecan shell derived biochar, the results indicated that although the biochar contained some N, mixing 0.5 % and 1.0 % biochar had no evident effect on the total C and total combustible nitrogen (TCN). However, adding 2 % biochar showed a considerable increase in the soil mean TCN content (Novak et al. 2009), although the soil N status was not significantly improved.

Chan et al. (2007) conducted glasshouse pot trial experiments where the agronomic benefits of greenwaste biochar applied as a soil amendment were investigated. Radish was planted in an acidic hardsetting soil with a low soil organic carbon content, and its dry matter production was later analyzed.

The DM production of radish using greenwastes and ammonium nitrate were investigated in the absence and presence of N fertilizer. It was found that in the absence of N fertilizer, biochar application did not at all cause an increase in the crop yield. However, increasing biochar application rates (10, 50 and 100 t ha^{-1}) resulted in significant yield increases in the presence of 100 kg ha^{-1} of N fertilizer. As the

biochar used in this study had a low N content (1.3 g kg^{-1}), negligible mineral N, and a high C:N ratio of 200, its application to the soil did not contribute to any additional available N to the crop. Therefore, it was shown that biochar has the potential to improve N fertilizer use efficiency of plants (Chan et al. 2007; Ding et al. 2010; Gaskin et al. 2008).

Steiner et al. (2008) used both charcoal and compost to determine the influence of on N retention on a permeable humid tropic soil. It was found that soil charcoal amendments enhanced the efficiency of mineral N fertilizer more than the compost. Furthermore, there was a significant recovery difference of 7.2 % between the total N recovered in soils with biochar and the control. This indicated an improvement in the fertilizer usage of N, P, and K.

Phosphorus

Soils found in tropical regions are particularly poor in plant available phosphorus resulting in P deficient environments. These soils contain sesquioxides that have the ability to strongly sorb phosphate (Turner et al. 2006), and thereby creating a sink on the availability of inorganic phosphorus for plants (Oberson et al. 2006). Sandy textured soils give biochar the potential to ameliorate P leaching in soils, therefore, it is expected that P will increase with increasing levels of biochar additions (Novak et al. 2009). In a study conducted on the response of DM production of radish using greenwastes, the biochar application increased the P concentration. It was established that significant yield increases were only found at biochar application rates greater than 50 t ha^{-1}, and when no N fertilizer was applied. This increase was due to the high concentrations of available P found in the biochar, and because P was no longer limiting (Chan et al. 2007).

Potassium

In a study conducted on the response of DM production of radish using greenwastes, the biochar application increased the K concentration. It was found that significant increases were only found at biochar application rates greater than 50 t ha^{-1} and when no N fertilizer was applied. This increase was due to the high concentrations of exchangeable K found in the biochar (Chan et al. 2007).

Calcium

The application of biochar increased the Ca concentration in a study conducted on the response of DM production of radish using greenwastes. It was found that significant increases were only found at biochar application rates greater than 50 t ha^{-1} and when no N fertilizer was applied (Chan et al. 2007). A field trial conducted over a period of 4 years with biochar application rates of 0, 8, and 20 t ha^{-1} respectively also showed an overall increase in available Ca. Over time, the available Ca content increased from 101 % to 320 % and up to 30 cm depths. These increases further meant that there was minimal Ca leaching with biochar (Major et al. 2010).

Magnesium

In a 6 week pot trial study conducted on the response of DM production of radish using greenwastes, the various biochar application rates were relatively similar in the Mg concentrations. It was found that significant reductions were only found in the unfertilized treatments at 10 t ha^{-1} and in the fertilized treatments at 50t ha^{-1} (Chan et al. 2007). In contrast, (Major et al. 2010) found that the available Mg content increased from 64 % to 217 % over a biochar application rate of 0-20 t ha^{-1}, and over a period of 4 years.

Sulfur

The common S functional groups for low temperature biochar are sulfonates and sulfates (Amonette and Joseph 2009). The pecan shell biochar study conducted by Novak et al. (2009) showed that exchangeable S marginally decreased with an increase in the biochar concentration that was added.

2.5.2 Micronutrients

Iron and Manganese

Iron (Fe) and manganese (Mn) are associated, and largely retained during biochar formation (Amonette and Joseph 2009). In the study carried out by Gaskin et al. (2008), the poultry litter biochar had the highest amount of Fe at 3.91 mg kg^{-1},

whereas the peanut hulls and pine chips biochars were significantly lower at 0.42 mg kg^{-1} and 0.13 mg kg^{-1} respectively.

In the pecan shell based biochar investigation carried out by Novak et al. (2009), the soil had increased Mn concentrations after the 67 day trial period. However, the water leachates contained reduced amounts of Mn. This demonstrates that Mn was largely retained during biochar formation due to its high association with a number of organic and inorganic forms in the biomass (Amonette and Joseph 2009). The investigation carried out by Gaskin et al. (2008) compared three different biochars. It was found that the poultry litter biochar had the highest amount of Mn concentrations at 377.0 mg kg^{-1}. The concentrations of Mn of the other two biochar substrates were smaller than the poultry litter, with reported values of 44.0 mg kg^{-1} for the peanut hulls and 13.8 mg kg^{-1} for the pine chips.

Zinc

The pecan shell biochar study conducted by Novak et al. (2009) showed that extractable Zn marginally decreased from 13 to 10 mg kg^{-1} with an increase in the addition of biochar concentration. This demonstrates that the biochar has a high sorption capacity for Zn. In a study where three different biochars were compared against each other, it was shown that the concentration of Zn showed great variety depending on which feedstock was used. The poultry litter biochar was much higher than the pine chips and peanut hulls biochars with reported values of 414 mg kg^{-1}, 47.8 mg kg^{-1}, and 20.2 mg kg^{-1}respectively (Gaskin et al. 2008).

Copper

The pecan shell biochar study conducted by Novak et al. (2009) showed that the copper (Cu) concentration was not significantly affected by biochar addition. Its results show that at 0.5% increments of biochar from no biochar addition to 2.0 %, the Cu concentration fluctuated around 0.7 mg kg^{-1} Cu. In contrast to the concentration of Cu in the biochar, the study conducted by Gaskin et al. (2008) showed high concentrations of Cu. The poultry litter biochar was reported as the highest as 381 mg kg^{-1}, whereas the peanut hulls and pine chips biochars were significantly lower at 36.5 mg kg^{-1} and 1.7 mg kg^{-1} respectively.

Molybdate

In the study conducted by Gaskin et al. (2008), the concentration of the heavy metal Molybdate (Mo) was reported as being low in all three different biochars. The greatest variation was observed in the pine chips biochar, with the lowest concentration at < 1.0 mg kg^{-1}, and the highest concentration was at 15.6 mg kg^{-1} as reported for the peanut hulls biochar.

2.5.3 Availability of non-essential elements, toxic heavy metals and metalloids

Although little research has been conducted on the possible toxic effects of biochar-amended soils, the potential effects associated with the presence of heavy metals and organic compounds condensed on the surface of biochar during pyrolysis are of concern (Joseph et al. 2010). Since biochar has a high sorption capacity (Laird 2008), it may influence the widespread distribution of persistent organic pollutions (POPs) particularly because they have shown prospective to serve as a sink when applied to soils. Therefore, considering the application of biochar to soil, the allocation of POPs may be altered to the extent whereby an understanding of the likely impact of biochar applications to soil on the accumulation of POPs is required and necessitates further investigation (Kookana et al. 2011).

Furthermore, it has been elucidated that a potential risk of contamination exists more pertinently when the biochar applied to soil is pyrolyzed from bio-waste feedstock such as sewage sludge, municipal waste, chicken litter and compost. This risk is primarily associated with the occurrence of harmful compounds such as PAHs and heavy metals (Verheijen et al. 2009).

Generally, heavy metals are common in household, municipal, or industrial wastes. All of these sources may be problematic because of land application of biochar resulting in contamination of the environment (Lehmann et al. 2006). Distinct to other soil amendments such as sewage sludge, biochar's longevity in soil reduces the prospect of heavy metal accumulation caused by repeated applications (Lehmann and Joseph 2009). However, a study conducted in Japan gave no evidence of toxic levels of heavy metals from sewage sludge produced biochar (Shinogi et al. 2003).

Beesley et al. (2010) performed a comparison study between biochar and greenwaste compost evaluating their effectiveness as soil amendments in multi-element contaminated soils. It was shown that although both amendments have the potential to act as soil conditioners, biochar was more effective for use than greenwaste compost. Biochar had a greater effect in reducing the concentration of the phytotoxic water soluble Cd and Zn, and total and bio-available PAH groups. Furthermore, biochar was able to increase shoot emergence, and Cu and Pb concentrations to a minimal degree. Therefore, biochar would be better suited to be used as remediation for contaminated land than compost.

In a similar study, Hartley et al. (2009) used three different arsenic (As) contaminated soils to evaluate the effects of greenwaste compost and biochar on the growth and uptake of As in *Miscanthus*. Both organic amendments had a negligible influence on the uptake of As into *Miscanthus* foliage. The minimal effects that biochar had on As mobility were attributed to a dual competition between P for binding sites and increases soil alkalinity. Although biochar was able to decrease soil acidity, it was found that the compost increased both available P and water soluble Fe and C in pore water, and thereby improved the mobility of As.

In a study based on biochar produced from dairy manure, Cao et al. (2009) made use of sorption isotherms to determine the mechanisms responsible for the removal of the heavy metal lead (Pb), and an organic contaminant, atrazine. In a comparison study between the biochar and activated carbon produced from woody plants used as a control, it was suggested that Pb had a higher sorption capacity for biochar than activated carbon. This was attributed to the occurrence of a combination of sorption-precipitation mechanisms. The sorption mechanism contributed to the surface sorption of Pb, characterized by L-type isotherms. Whereas, the precipitation mechanism was responsible for the retention of Pb by the biochar. Spectroscopic analyses by X-ray diffraction (XRD) and Fourier transmission infrared (FTIR) showed that the removal of Pb by biochar was due to the formation of a Pb-phosphate precipitate. In comparison, atrazine showed a linear isotherm, characteristic of solute partitioning. As a result of the different sorption isotherms demonstrated by Pb and atrazine, there was negligible competition between their sorption capacities. Therefore, it was concluded that biochar produced from dairy manure is a positive

sorbent for the removal of lead and atrazine. However, it still remains that a comprehensive and careful risk assessment for possible contaminants is still necessary in order to fully understand the likely contaminant toxicity associated with biochar feedstock type, pyrolysis conditions and application levels (Verheijen et al 2009).

2.6 Carbon sequestration

Terra preta soils contain large carbon reservoirs as studies indicate that up to 70 times more carbon has been found in these soils in comparison to surrounding Oxisols (Glaser et al. 2001). Although afforestation still remains a feasible way of sequestering carbon by photosynthesis, the process is only carbon neutral. In contrast, the application of biochar to soils has the added advantage of turning carbon sequestration into a carbon negative system (Lehmann 2007b). This means that, because biochar is very slow to decompose, and yields a high carbon output over time, it is an effective, viable and sustainable C sequestration option (Vaccari et al. 2011).

Literature gives evidence that the application of biochar for carbon sequestration in agricultural soils is a feasible option for achieving climate change mitigation (Major et al. 2009; Sohi et al. 2010; Vaccari et al. 2011). Since biochar has been proposed to draw CO_2 from the atmosphere, and because considering that methane (CH_4) and nitrous oxide (N_2O) greenhouse gas emissions are generally high, and pose a huge threat globally to agricultural management, the potential effect of biochar has also been proposed as significant in dealing with greenhouse gas emissions (Sohi et al. 2010).

As most cultivated agricultural soils are depleted of soil organic carbon (Vaccari et al. 2011), amendment with biochar may provide the benefits of being long-term sinks for the withdrawal of carbon dioxide (Lehmann 2007b; Sohi et al. 2009), and further producing large amounts of renewable bio-energy (Laird et al. 2009). Lehmann (2007b) suggests that the pyrolysis of inexpensive feedstock can also contribute to emissions reductions when the pyrolysis gases are captured for bio-energy production. Cumulatively, these advantages serve as efficient means for climate change mitigation (Sohi et al. 2009). However, the exclusive use of biochar is not suggested. Instead, as an all-encompassing strategy, it is recommended that biochar

be used in conjunction with alternate climate change mitigation strategies to help in better reducing greenhouse gas emissions (Lehmann 2007a; Verheijen et al. 2009).

Biological feedstocks with large lignin concentrations have been reported to possess a high C recovery and mineral content (NikAzar et al. 1997; Raveendran et al. 1995). This is demonstrated in a study conducted by Novak et al. (2009) where it was shown that no significant loss of soil organic carbon took place during incubation studies of pecan shell derived biochar. Instead, the soil had an increase of 11.8 g C kg^{-1} after being mixed with a level of 2 % biochar, and thus suggesting that the addition of biochar has the potential to efficiently sequester C.

Decomposition of biochar occurs at different rates and by different processes, and is dependent on the feedstock and pyrolysis conditions (Zimmerman 2010). The degradability of the feedstock is dependent on the recalcitrant nature of biochar, and can be influenced by biological and chemical conditions (Glaser et al. 2001). However, black carbon rich soils can be decomposed over time by abiotic and microbial oxidation (Cheng et al. 2006; Zimmerman 2010).

The compounded effects of an increasing global population, diminishing food reserves and climate change are a global growing concern (Lehmann and Joseph 2009). Since food security partly depends on the sustainability of good agricultural soil practices, Whitman and Lehmann (2009) suggested that soil-biochar amendments could most likely contribute towards improved agronomic and environmental developments and the alleviation of climate change. Further, considering that CO_2, CH_4 and N_2O pose a major threat to global warming (Lehmann et al. 2006), the effect of biochar to contain and potentially reduce these emissions warrants further investigation as the current evidence has been sparsely assessed (Sohi et al. 2010). In addition, because the climate is generally still becoming dryer, it is unlikely that biochar could solely alleviate crop production concerns. Therefore, alternatives such as crop varieties that could withstand lower rainfall and higher temperatures should also be assessed in future research.

2.7 Conclusions

The increasing problems of food insecurity, global climate change and low nutrient-holding soils greatly affect the rising human population. In particular, degraded agricultural soils that are acidic, infertile, comprising mostly of kaolinitic clay, and requiring multiple synthetic chemical applications further exacerbate the crisis of decreasing crop yields. Effective amendment of such soils using pyrolyzed biomass therefore necessitates research into the use of biochar in agricultural soils.

Biochar has been proposed to aid in increased agricultural productivity due to some of its positive attributes. Its effects when applied on acidic soils have shown positive contributions through increases in pH, organic carbon, and exchangeable basic cations. Further, biochar application as a soil amendment has the potential of contributing to carbon sequestration and renewable energy approaches. This suggests that biochar can be used as a climate change mitigation strategy.

There are, however, possible negative effects attributed to the application of biochar to soils which would require caution. Since biochar influences the availability of N in soils and subsequently crops, the weathering of biochar results in N immobilization, which generally tend to induce N deficiencies in crops. Also, the immediate increase in soil pH following biochar addition may cause crop micronutrient deficiencies. Lastly, because contaminants such as organic compounds and heavy metals may be present in some biochars, feedstock material needs to be carefully considered prior to pyrolyzing biomass.

The effects of specific biochars on specific soils need to be thoroughly evaluated to improve the efficacy of the use of biochar in agricultural soils. Literature shows that biochar application as a soil amendment may contribute in climate change mitigation and carbon sequestration. Furthermore, careful consideration is necessary on the type of biochar applied to soil because the biochar properties such as pH and nutrient availability are highly dependent on the feedstock and pyrolysis conditions under which biochar is produced.

CHAPTER 3

3 Biochar Amendment of Infertile Sandy Soil (Western Cape, South Africa): Effect on Soil Chemical Properties and Wheat Growth

3.1 Introduction

Biochar addition to soils has a multitude of potential agricultural benefits. These include liming of acid soils, addition of basic cations and micronutrients, improving water holding capacity, and a gradual release of nutrients to the growing plant (Glaser et al. 2002; Laird et al. 2010; Sohi et al. 2010; Van Zwieten et al. 2010a). Leached sandy soils typically have low soil pH values, poor buffering capacities, low cation exchange capacity (CEC), with values ranging from 2-8 $cmol_c\ kg^{-1}$, and can have Al toxicity (Novak et al. 2009). The addition of biochar to these highly leached, infertile soils gives an almost immediate increase in the availability of some basic cations (Glaser et al. 2002; Liang et al. 2006), as well as a significant improvement in crop yields, particularly where nutrient resources are in short supply (Lehmann and Rondon 2006). Over time, these additions continue to promote soil nutrient availability by giving rise to greater stabilization of organic matter and a subsequent reduction in the release of nutrients from organic matter (Glaser et al. 2001; Lehmann and Rondon 2006).

Biochar nutrient content variation can be attributed to different feedstocks and different pyrolysis conditions (Chan and Xu 2009; Schmidt and Noack 2000). The total elemental contents of an organically bound nutrient such as nitrogen (N) does not necessarily reflect its actual availability to growing plants (Chan and Xu 2009; Havlin et al. 2005). For example, biochar feedstock greatly influences total N and phosphorus (P) contents because both mineral N (ammonium- and nitrate N) and available P are usually more in biochars produced from feedstocks of animal origin, than those of plant origin (Chan and Xu 2009). Also, since only a small fraction of N is relatively easily mineralizable, it is likely that biochar application may result in lower N uptake (Rondon et al. 2007). In contrast, biochars typically have high total and available potassium (K), which has been shown to result in increased K uptake (Chan et al. 2007; Lehmann et al. 2003).

Further, Lehmann et al. (2003) attributed the increased plant growth responses observed to greater plant uptake of K, P, Ca, Zn and Cu with increasing biochar applications. In a study conducted by Vaccari et al. (2011) positive effects on the growth, yield and grain quality of durum wheat were observed when a large scale application of biochar was made. It was suggested that 30 and 60 t ha^{-1} biochar applications might concurrently increase C sequestration and contribute to successful renewable energy production while ameliorating agricultural soils.

Plant-based materials consist of various N containing structures that include amino acids, amines, and amino sugars. When subject to pyrolysis, these structures get condensed and form heterocyclic N aromatic structures (Cao and Harris 2010; Koutcheiko et al. 2006), thus converting the N to a form which may not be available for microbial and ultimately plant use (Gaskin et al. 2010). Consequently, the residual N in the biochar is largely found as recalcitrant heterocyclic N rather than bio-available amine N (Cao and Harris 2010; Novak et al. 2009). Fortunately, there is a beneficial interaction when biochar is applied together with a N fertilizer (Chan et al. 2007; Steiner et al. 2008), giving rise to improved fertilizer use efficiency. This makes it economically viable due to the reduction in the amount spent on commercial mineral fertilizers (Steiner et al. 2008).

As a consequence of biochar's liming value, a positive response was observed in plant biomass production (Lehmann et al. 2003; Rondon et al. 2007; Vaccari et al. 2011; Van Zwieten et al. 2007). In particular, Van Zwieten et al. (2010b) observed significant increased bread wheat growth averaging about 2.5 fold more than the control when papermill biochar with fertilizer was applied to an acidic, highly weathered soil. The lime (as carbonates) in the biochar decreased the availability of Al to below detection. In contrast, negative yield responses have also been found. Kishimoto and Sugiura (1985) and Mikan and Abrams (1995) reported yield reductions induced by micronutrient deficiencies caused by increasing soil pH.

Understanding the chemical changes that occur in biochar-amended soils is of great importance to managing and applying biochar in soils. Many studies have been conducted on the application of biochar to soils; however, there is a current scientific gap in knowledge of this application to South African soils. We selected sandy, acidic soils for this study because they are common in the Western Cape and are typically

leached, infertile, with poor nutrient and water holding capacities, and therefore are soils that would potentially benefit from biochar amendment. We chose pinewood biochar as the dominant type of biochar it is readily available on the South African market. Wheat was selected as a model crop as it widely cultivated in the Western Cape Province.

The study consisted of two parts. In the first experiment, wheat was grown for 12 weeks and compared the effect of biochar in unfertilized and fertilized treatments. The second experiment only looked at the effect of wheat growth in fertilized treatments and was harvested at maturity.

3.2 Objectives

The primary objective of this study was to investigate the effect of applying varying levels of locally produced biochar on acidic, sandy Western Cape soil on soil chemistry, growth and nutrient uptake of wheat. The aim of this investigation is to elucidate the soil chemical mechanisms behind the positive and/or negative plant growth responses to the addition of biochar.

Ultimately, the aim was to determine the optimum application level of biochar to the sandy soil to obtain improved soil fertility and maximum plant growth.

3.3 Materials and methods

3.3.1 Soil and biochar collection and preparation

A low potential, acidic, sandy soil was collected from a fallow field (covered with kikuyu grass and weeds) in Brakenfell, Western Cape (33° 53’ 43.08’’ S, 18° 43’ 24.24’’ E). Only the E horizon was collected to a depth of 1 m after clearing the top 10 cm of the soil surface. The soil texture was classified as a pure sand (97.1 % sand, 2.6 % silt, 0.3 % clay) of a medium sand grade. According to the South African soil taxonomic system (Soil Classification Working Group 1991) the soil classifies as a Kroonstad form in the Morgendal family, which is characterized by thick bleached A and E horizons overlying a clay layer at a depth below 1 m with signs of wetness. According to the World Reference Base (IUSS Working Group WRB) classification system (IUSS Working Group WRB 2006) the soil is classified as a Haplic Stagnosol (Albic). The soil was air-dried and sieved (<2 mm) prior to experimental use.

The biochar used in this study was produced from pinewood sawmill waste by a small-scale commercial producer from the Eastern Cape, South Africa. The sawmill wastes were slow pyrolyzed at approximately 450 °C, and then crushed. Sieved biochar (<2 mm) was mixed and thoroughly homogenized with the sandy soil using a cement mixer to make up the four application levels of 0.05, 0.5, 2.5, and 10.0 % biochar (w/w) (Table 1.1).

Table 1.1 Application levels of biochar used in the pot trial

Percentage (%) (w/w)	0.05	0.5	2.5	10.0
Approximate g biochar kg^{-1} soil	0.5	5.0	25.0	100.0
Approximate tons ha^{-1} (15 cm depth)	1.0	10.0	50.0	200.0

3.3.2 Chemical and physical characterization of the biochar

The biochar was oven dried at 40 °C for 12 hours and then ball milled to less than 1 mm diameter particle size. The pH of the biochar was measured using a Metrohm 827 Lab pH meter by the method described by Cheng and Lehmann (2009) which makes use of a 1:20 biochar to solution ratio using distilled water and 1 M potassium chloride (KCl). This 1:20 ratio is used on account of the low bulk density of the biochar (approximately 0.4 g cm^{-3}) and is approximately volumetrically equal to a 1:2.5 soil to solution ratio (Cheng and Lehmann 2009). Biochar exchangeable acidity (EA) was determined according to the potassium chloride method in a 1:20 biochar to 1 M KCl solution ratio (Thomas 1982). Total C, hydrogen (H) and N contents were determined by dry combustion using the EuroVector Elemental Analyzer 3000 series (Nelson and Sommers 1996). The percentage oxygen was determined by subtraction of C, N, H, ash and moisture content from the total mass of the biochar sample. Exchangeable cations were determined using 1 M ammonium acetate (NH_4OAc) at pH 7 (Thomas 1982). Water-soluble cations and anions, electrical conductivity (EC) and pH were determined for the biochar using a 1:20 biochar to distilled water ratio. The Jenway 4510 Conductivity Meter was used for EC. Cation exchange capacity (CEC) was determined according to the method for arid-land soils as described by Rhoades (1982). This method was selected due to the alkaline nature of the biochar. It entails saturation of cation exchange sites with sodium (Na), followed by an extraction with magnesium nitrate ($MgNO_3$). The biochar surface

acidity and basicity were measured by base and acid adsorption respectively. This was carried out according to the method described by Cheng and Lehmann (2009), which is based on the Boehm titration method for characterizing carbon blacks and other carbons (Boehm 1994). The Boehm titration results were also used to estimate the liming potential of biochar, in terms of its calcium carbonate equivalence. Plant available P and other macro- and micronutrients were determined in the biochar using the ammonium bicarbonate (AB) diethylenetriamine pentaacetic acid (DTPA) method (Soltanpour and Schwab 1977). This method was selected due to the alkaline nature of the biochar and because it can be used to determine plant available P and other elements simultaneously in the extracting solution using inductively coupled plasma mass spectroscopy (ICP-MS) using the Thermo ICap 6300 radial instrument. All determinations were carried out in duplicate.

Proximate analysis was carried out on the biochar using thermal gravimetric analysis (TGA) to determine the moisture, volatiles, ash and fixed carbon contents (ASTM standard 1762-84 2007). Brunauer-Emmett-Teller (BET) specific surface area (SSA) of the biochar was determined using nitrogen gas on Micrometrics ASAP 2010 system.

Biochar total elemental composition was determined using X-ray Flourescence (XRF) Spectrometry (Loeppert and Inskeep 1996). The biochar sample water loss was determined at 110 °C. A 1.0 g biochar sample, thoroughly mixed with 10.0 g fused anhydrous lithium borates with lithium iodide (Claisse) was used to prepare glass beads by fusion for the analysis of major elements using the XRF Rh tube. The loss of ignition (LOI) was also determined on the glass bead sample at 1000 °C. The biochar trace element analysis was carried out on a pressed pellet by using 8.0 g of sample, thoroughly mixed with 0.5 g of Moviol, a wax-based binder. The element chemical analyses were subsequently carried out by XRF on the PANalytical Axios spectrometer.

Fourier Transform Infrared (FTIR) spectroscopy was used to identify both crystalline and poorly crystalline minerals on the biochar. The FTIR analysis was carried out with 64 scans on a 0.5 % (oven dry weight equivalent) pressed potassium bromide (KBr) pellet (Johnston 1996). The IR spectra was performed using a Thermo Nicolet

Nexus™ FTIR spectrophotometer, and processed using the OMNIC version 7.2 software.

3.3.3 Characterization of the soil and soil-biochar mixtures before planting

The pH of the soil and soil-biochar mixtures was measured in distilled water and 1 M KCl in a 1:2.5 soil to solution ratio (White 1997) using a Metrohm 827 pH meter. The potassium chloride method was used to determine exchangeable acidity on the soil and soil-biochar mixtures in a 1:2.5 ratio using a 1 M KCl solution (Thomas 1982). Total C and N content of the soil and soil-biochar mixtures was determined by dry combustion using the EuroVector Elemental Analyzer 3000 series. Exchangeable cations were determined using 1 M ammonium acetate (NH_4OAc) at pH 7.0 (Thomas 1982). The water-soluble cations (Ca, Mg, K and Na) and anions (Cl, NO_3, PO_4 SO_4) were determined in a 1:5 water extract by Atomic Absorption Spectrometry (AAS), and Ion Chromatography (IC), respectively. Electrical conductivity and pH of the soil and soil-biochar mixtures were determined in a 1:5 soil water extract. The plant available P content of the sand was determined using Bray 2 (0.1 M HCl and 0.03 M NH_4F) extraction method using a 1:7.5 soil to solution ratio (Kuo 1996). Plant available P and macro- and micronutrients were determined in the soil and soil-biochar mixtures using the AB-DTPA method (Soltanpour and Schwab 1977). The soil and biochar particle-size analysis (PSA) was determined according to the pipette method as described by Gee and Bauder (1986). All determinations were carried out in duplicate.

3.3.4 Wheat pot trial

Winter wheat (*Triticum aestivum* L.) was grown in nursery pots (21 cm height, 25 cm top diameter and 7.1 L volume) containing soil and soil-biochar mixtures (6.0 kg oven dry equivalent) in a greenhouse tunnel at Stellenbosch University's experimental farm, Welgevallen from June 2010 to September 2010. The pots were lightly packed to a bulk density of approximately 1.5 g cm^{-3}. The pots were arranged in a randomized complete block design. The pot trial investigated the effect of four different levels of biochar (0.05, 0.5, 2.5 and 10.0 % biochar w/w) with and without the addition of a water-soluble broad spectrum fertilizer on the growth and nutrient uptake of the wheat up until a period of 12 weeks from planting. There were 4 replicates per treatment, and therefore a total of 40 measurements for the study.

Each of the fertilized pots received the same amount of fertilizer which was based on the macro-and micronutrient recommendations for winter wheat grown on sandy soils in the Western Cape Province as supplied by the Department of Agronomy, Stellenbosch University (Table 1.2). The fertilizer was made up using Chemicult Hydroponic Nutrient Powder (Starke Ayers, South Africa), mono-ammonium phosphate and ammonium nitrate. Fifty percent of the fertilizer was added at planting, and the remaining portion was added in a split application at 4 and 8 weeks. Ten pre-treated wheat seeds were sown to a depth of approximately 20 mm in each pot. Following germination, the seedlings were thinned, and the healthiest 4 plants were retained in each pot. Irrigation was applied weekly to field capacity. The percent (%) water retention (field capacity) of the various treatments was as follows: Control = 0.0; 0.05 % = 0.6; 0.5% = 2.3; 2.5 % = 10.9; 10.0 % = 35.6. Weekly water use measurements were taken throughout the duration of the pot trial, and weekly leaf length measurements were taken from the third week of growth until harvest.

3.3.5 Wheat growth post-harvest determinations

Following harvest at 12 weeks, total green leaf area, total dry above- and below ground matter production, soil pH, and total plant nutrient content were determined. The above ground plant matter comprised of leaves, stems and ears of wheat. Leaf area of the green leaves was measured per plant using a leaf area meter (LI-COR Model 3100). Thereafter, the above-and below ground plant matter was washed in distilled water and oven dried at 70°C to a constant weight to determine the total dry matter production (yield). The pH of the post-harvest soil and soil-biochar mixtures was measured in both distilled water and 1 M KCl solution (1:2.5). Leaf samples of the whole plant were ground into fine powder and the leaf macro- and micronutrient contents were determined by acid digestion and ICP-OES. Total organic N was determined by the Kjeldahl method (Bremner 1996). Wheat nutrient analysis was performed at the Cape Institute for Agricultural Training: Elsenburg. The total nutrient uptake of the different elements was determined as a function of the wheat dry biomass production.

For the wheat pot trial grown to maturity, the ears of wheat were gently separated from the stems, and the wheat grain was removed from the ears by hand. Grain yield was determined on a dry weight basis. Grain N content was determined using the Kjeldahl method (Bremner 1996). Phosphorus and K contents were determined by

ICP. The grain protein content was determined according to the method described in the Handbook of feeds and plant analysis (AgriLasa). The method comprised digesting the dry grain with 50 mL sulfuric acid (H_2SO_4) and 2 kjeltabs. This was followed by the addition of water, distillation and titration with hydrochloric acid (HCl).

The statistical analysis was performed using SAS Enterprise Guide 4. A one-way analysis of variance (ANOVA) was used and significant differences between treatments were distinguished at the $P < 0.05$ level using Tukey's Studentized Range Test.

Table 1.2 Fertilizer nutrient levels used for the wheat pot trial.

Macronutrients	kg ha^{-1}	Micronutrients	g ha^{-1}
N	130	Fe	865
P	50	Mn	138
K	75	B	138
Ca	40	Zn	29
Mg	13	Cu	12
S	43	Mo	6

3.4 Results and discussion

3.4.1 Characterization of biochar

The biochar was alkaline in nature as indicated by the pH in distilled water (H_2O) (9.39) and KCl (8.57) (Table 1.3). This is due to the formation of ash during the pyrolysis process, which typically consists of Ca, Mg, K and Na carbonates (Yuan et al. 2011a). The XRD analysis also confirmed the presence of high carbonates (Table 1.9). The calcium carbonate equivalence (CCE) of the biochar is 1.3% (as calculated based on the Boehm titration results). Proximate analysis of the biochar showed that the moisture content was 2.61 % by mass, while the ash content, volatiles, and fixed C contents were 3.04, 19.90, and 74.45 % respectively (Table 1.4). The fixed carbon content indicates the portion of the biochar that consists of condensed aromatic rings (black C) and is likely to persist in soils, whereas, the volatile component is more easily degraded by soil microorganisms, depending on its physical accessibility

(Keiluweit et al. 2010). The proximate analysis results are in agreement with the high total C content (82.7 %) of the biochar (Table 1.3).

Table 1.3 The total C and N contents, and pH values as measured in distilled H_2O and 1 M KCl of the soil, soil-biochar mixtures and biochar before planting.

% Biochar (w/w)	% C	% N	C:N ratio	pH (H_2O)	pH (KCl)
0	0.16 c	0.03 b	5.3 b	5.14 f	4.30 e
0.05	0.33 c	0.05 b	6.6 b	6.32 e	5.54 d
0.5	0.70 c	0.05 b	14.0 b	6.80 d	5.82 d
2.5	1.93 c	0.13 b	14.8 b	7.34 c	6.55 c
10.0	8.27 b	0.14 b	59.1 ab	8.42 b	7.50 b
Biochar	82.71 a	0.53 a	156.1 a	9.39 a	8.57 a

Means in the same column followed by the same symbol are not significantly different at $P < 0.05$ level based on Tukey's Studentized Range test.

Table 1.4 Proximate analysis determined using TGA and percentage C, O+S, N, and H (expressed as % of total dry weight).

% Volatiles	% Fixed C	% Ash	% C	% O	% N	% H	C:N	O/C	H/C
19.90	74.45	3.04	82.71	11.11	0.53	2.95	156:1	0.13	0.04

The surface acidity and surface alkalinity of the biochar as determined by Boehm titration was 0.73 and 0.25 mmol g^{-1}, respectively. These values are similar to previously reported values of relatively aged (oxidised) biochar (Cheng and Lehmann 2009). The CEC (pH 7) of the biochar as determined by the Rhoades method was 34.3 $cmol_c$ kg^{-1}, which is much lower than the typical CEC of humified organic matter which is around 200-300 $cmol_c$ kg^{-1} (Sparks 2003). The biochar had a relatively high BET specific surface area of 346.42 m^2 g^{-1}. These characteristics are typical of biochar derived from woody material pyrolyzed at temperatures above 400 °C (Keiluweit et al. 2010). The O/C and H/C atomic ratios (Table 1.4) are characteristic for wood-based biochars produced at temperatures above 400 °C (Keiluweit et al. 2010). Spokas (2010) suggests that an O/C atomic ratio < 0.2 may provide a half-life of at least 1000 years, and thereby give evidence that biochar has great potential for long-term C sequestration (Lehmann et al. 2006). The extremely

low H/C ratio suggests that the biochar loses hydrogen as the carbon forms highly stable, condensed aromatic structures (Van Zwieten et al. 2010b).

Table 1.5 shows that the dominant exchangeable cations in biochar are Ca and K, and that biochar reduced the EA and acid saturation content. The biochar contains considerable amounts of water-soluble cations, such as Na^+, K^+ and Ca^{2+}, and anions, such as SO_4^{2-}, and Cl^- (Table 1.6). In addition, the biochar appears to contain generous amounts of AB-DTPA plant available macro- and micronutrients (Table 1.7), similar to the low mineral ash green waste biochar studied by Van Zwieten et al. (2010a). There was no noteworthy heavy metal contamination found (Table 1.8).

Table 1.5 The exchangeable base cations, exchangeable acidity (EA), effective cation exchange capacity (ECEC), % acid saturation and exchangeable sodium percentage (ESP) of the soil, soil-biochar mixtures and biochar before planting.

% Biochar (w/w)	Cations ($cmol_c\ kg^{-1}$)				EA ($cmol_c\ kg^{-1}$)	ECEC ($cmol_c\ kg^{-1}$)	% Acid saturation	ESP
	Ca	Mg	K	Na				
0	1.14 c	0.12	0.03 c	0.18 b	0.50 b	1.96 b	25.51 a	8.99 a
0.05	1.37 bc	0.13	0.05 c	0.18 b	0.13 b	1.86 b	6.99 b	9.61 a
0.5	1.34 bc	0.13	0.09 c	0.18 b	0.10 b	1.84 b	5.43 bc	9.95 a
2.5	1.48 bc	0.17	0.14 c	0.21 b	0.05 b	2.04 b	2.45 bcd	10.43 a
10.0	1.60 b	0.27	0.41 b	0.26 b	0.03 b	2.57 b	1.17 bc	10.07 a
Biochar	4.75 a	1.35	3.74 a	1.05 a	0.00 a	10.90 a	0.0 d	9.66 a

Means in the same column followed by the same symbol are not significantly different at $P < 0.05$ level based on Tukey's Studentized Range test.

Table 1. 6 Water-soluble cations and anions extracted from of the soil, soil-biochar mixtures (1:5 extracts) and biochar (1:20 extract)

% Biochar (w/w)	EC (dS m^{-1})	Cations (mg kg^{-1})				Anions (mg kg^{-1})			
		Ca	Mg	K	Na	Cl	NO_3	PO_4	SO_4
0	0.061 d	13.5 bc	3.0 cd	11.5 b	28.3 b	24.0 a	26.0 a	0.0 a	16.0 a
0.05	0.071 d	21.5 b	2.8 d	19.8 b	58.0 b	38.0 a	17.3 a	2.8 a	33.8 a
0.5	0.090 c	9.8 c	2.8 d	20.3 b	64.3 b	51.5 a	30.8 a	2.3 a	36.5 a
2.5	0.090 c	13.5 bc	3.8 c	36.8 b	48.5 b	49.5 a	23.3 a	4.3 a	29.5 a
10.0	0.152 b	19.8 b	6.0 b	97.3 b	65.3 b	72.3 a	21.5 a	1.3 a	38.3 a
Biochar	0.754 a	73.0 a	70.0 a	3070.0 a	782.0 a	601.0 a	30.0 a	0.0 a	465.0 a

Means in the same column followed by the same symbol are not significantly different at $P < 0.05$ level based on Tukey's Studentized Range test.

Table 1.7 Soil, soil-biochar mixtures and biochar AB-DTPA plant available macro-and micronutrients.

% Biochar (w/w)	Macro- and micronutrients (mg kg^{-1})											
	P*#	Ca	Mg	K*	Fe*	Mn*	Cu*	Zn*	Co	B	Mo
0	3.94 d	56.02 e	13.33 e	10.88 d	30.88 b	0.106 f	0.188 a	0.443 b	0.006 e	0.106 a	0.010 a
0.05	7.53 c	187.34 d	16.15 d	13.96 d	32.27 b	0.752 d	0.254 a	1.542 b	0.010 b	0.076 a	0.009 a
0.5	7.81 c	190.17 d	16.71 d	20.40 d	29.45 bc	0.675 e	0.254 a	1.173 b	0.008 cd	0.058 a	0.024 a
2.5	8.82 bc	208.20 c	22.12 c	56.86 c	29.47 bc	0.914 c	0.313 a	1.364 b	0.009 bc	0.074 a	0.017 a
10.0	11.18 b	254.82 b	38.93 b	161.47 b	26.72 c	1.392 b	0.538 a	1.710 b	0.007 de	0.056 a	0.013 a
Biochar	89.59 a	1432.49 a	301.37 a	1720.85 a	42.88 a	11.327 a	8.793 a	9.789 a	0.016 a	0.442 a	0.050 a

*Critical values (mg kg^{-1}) for the AB-DTPA test as taken from Soltanpour and Follett (1991): P: >15.0, K: 180, Fe: > 5.0, Mn: > 5.0, Cu: >2.0, and Zn: >1.5

#Bray 2 plant available P in (acidic) control soil determined as 11.07 mg kg^{-1}. Critical level for Bray 2 is 25 mg kg^{-1}.

Table 1.8 Soil, soil-biochar mixtures and biochar AB-DTPA plant available non-essential elements and toxins.

% Biochar (w/w)	Non-essential elements and toxins (mg kg^{-1})							
	Na	Al	Se	Cr	As	Ni	Pb	Cd
0	17.56 bc	32.71	0.011 a	0.041 b	0.028 e	0.033 b	0.169 a	0.002 b
0.05	13.65 c	35.50	0.022 a	0.055 b	0.038 de	0.035 b	0.278 a	0.004 b
0.5	15.49 bc	33.78	0.021 a	0.055 b	0.049 d	0.031 b	0.246 a	0.005 b
2.5	16.02 bc	31.80	0.030 a	0.067 b	0.118 c	0.045 b	0.246 a	0.004 b
10.0	24.06 b	26.84	0.021 a	0.083 b	0.359 b	0.029 b	0.210 a	0.005 b
Biochar	126.39 a	19.73	<0.000 a	1.921 a	5.371 a	0.123 a	0.857 a	0.026 a

Means in the same column followed by the same symbol are not significantly different at P < 0.05 level based on Tukey's Studentized Range test.

Table 1.7 Biochar elemental composition as determined by XRF spectroscopy.

Macro- and micronutrients (%)		Non-essential elements and toxins (%)	
Element	Concentration	Element	Concentration
P	0.09	Na	0.09
Ca	2.09	Si	0.76
Mg	0.21	Al	BD
K	1.64	Ba	0.001
S	0.14	Cr	0.011
Fe	1.11	Ni	0.001
Mn	0.03	V	0.000
Cu	BD	Pb	0.007
Zn	0.002	Ti	0.015
Co	BD	Ga	0.000

The FTIR spectrum (Fig. 1.1), showed a high peak of O-H stretching at approximately 3400 cm^{-1} (Keiluweit et al. 2009). The slight, yet considerable peak between 2935 and 2885 cm^{-1} may be attributed to the presence of aliphatic C-H stretching. The multiple peaks from 1600-700 cm^{-1} indicate the possible presence of cellulosic and ligneous components. Carboxylic carbon (C=O) and aromatic carbon (C=C) stretching vibrations were observed between 1700 and 1500 cm^{-1}. There was additionally greater evidence for aromatic C with the appearance of peaks between 885 and 750 cm^{-1}, due to the out of plane deformations of aromatic C-H (Keiluweit et al. 2010).

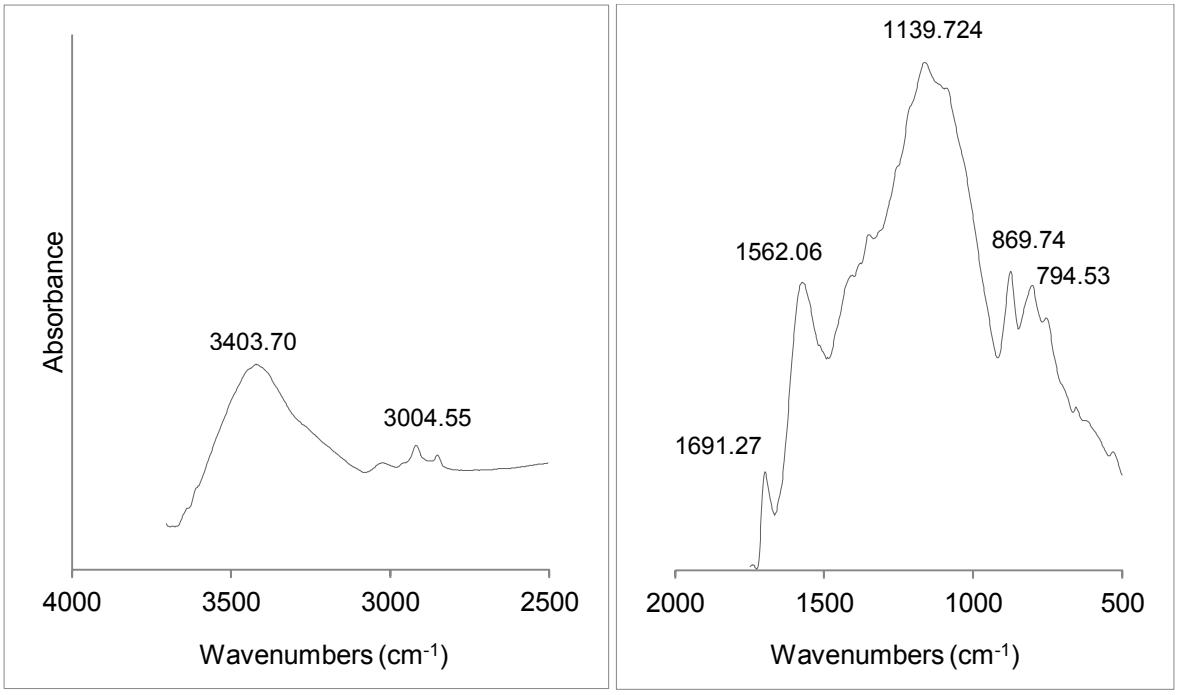


Figure 1.1 FTIR spectrum of the pine sawmill waste derived biochar.

3.4.2 Characterization of soil and soil-biochar mixtures before planting

The sandy soil used in this study was acidic with a pH of 5.14 in water and 4.30 in KCl (Table 1.3). The addition of biochar had a significant effect on increasing the soil pH at application levels from 0.5 % and higher (Table 1.3). The 10.0 % biochar treatment actually resulted in over-liming of the soil as it raised the pH of the soil to above pH 8 (in water). The problem is that the sandy soil is not well-buffered against pH changes (Tryon 1948) due to its low clay and organic matter content.

The addition of biochar to the soil resulted in an increase in exchangeable basic cations (Table 1.5), especially Ca and K, and increased the C:N ratio of the soil (Table 1.4). These results were similar to studies performed by Tryon (1948) with sand and hardwood charcoal, which showed increases in effective cation exchange capacity (ECEC) and exchangeable bases. The addition of biochar also increased the levels of water extractable cations especially Na and K (Table 1.6). This is probably due to the higher water solubility of Na and K carbonates and salts, compared to Ca and Mg carbonates or salts (McBride 1994). Thus, the reason behind the pH increase is the occurrence of dissolution reactions of the alkaline minerals (Lehmann et al. 2011), whereby a pH increase in the water-film around the biochar particles occurs (Joseph et al. 2010). The EC values of the soil, soil-biochar

mixtures and biochar are relatively low (Table 1.6) and thus do not suggest problems with soluble salts. The biochar applications did not significantly affect the levels of water extractable nitrates or phosphates (Table 1.6). The Bray 2 extractable P of the control soil (no biochar added) was 11.07 mg kg^{-1}, thus indicating that it was highly P deficient. The ammonium bicarbonate-DTPA plant available elemental extraction showed an increase in the macronutrients. The extractable P, Ca, Mg and K all increased with each level of biochar additions (Table 1.7). Since acidic soils are relatively deficient in P, Ca and Mg, which can limit crop growth and reduce crop yield, an increase in these macronutrients is favourable. The increase in plant extractable K can be ascribed to the very high K content in the pine wood biochar, as observed in the water-soluble K content.

It is also evident that many of the AB-DTPA extractable micronutrients were deficient in soil and soil-biochar mixtures (Table 1.7). For example, the availability of iron (Fe) decreases at increasing biochar application levels. According to the AB-DTPA threshold values published by Soltanpour and Follett (1991), the plant available manganese (Mn) and copper (Cu) are below the critical values for all treatments, although biochar still increases their availability. However, adding biochar reduced the availability of boron (B). This is probably because the availability and uptake of B decreases at high pH values. There was no noteworthy heavy metal contamination induced by biochar amendment to the soil (Table 1.8) based on the upper limit levels reported in Pais and Jones (1997).

3.4.3 Wheat pot trial harvested at 12 weeks

3.4.3.1 Effect of biochar on wheat leaf growth

Germination of all the wheat seeds had taken place by the second week after planting, and there were no visible differences in seedling germination and emergence between the biochar-amended and control pots. Weekly leaf length measurements were taken from the third week of growth until a week before harvest (Fig. 1.2). All of the unfertilized treatments showed a substantial weekly increase in leaf length throughout the biochar application levels except for the 10 % treatment, which grew at a slower pace in comparison to the control. However, the 2.5 % treatment differed significantly relative to the control (Fig. 1.2a). The fertilized treatments showed marginal increases in weekly leaf length measurements up until

the seventh week (Fig. 1.2b). Thereafter, very little leaf length growth occurred until harvest. Van Zwieten et al. (2007) found comparable results in a wheat pot trial using paper mill sludge biochar applied at 10 t ha^{-1} whereby a 30 - 40 % wheat height increase was observed on an acidic soil. The increase was primarily attributed to the liming potential of biochar.

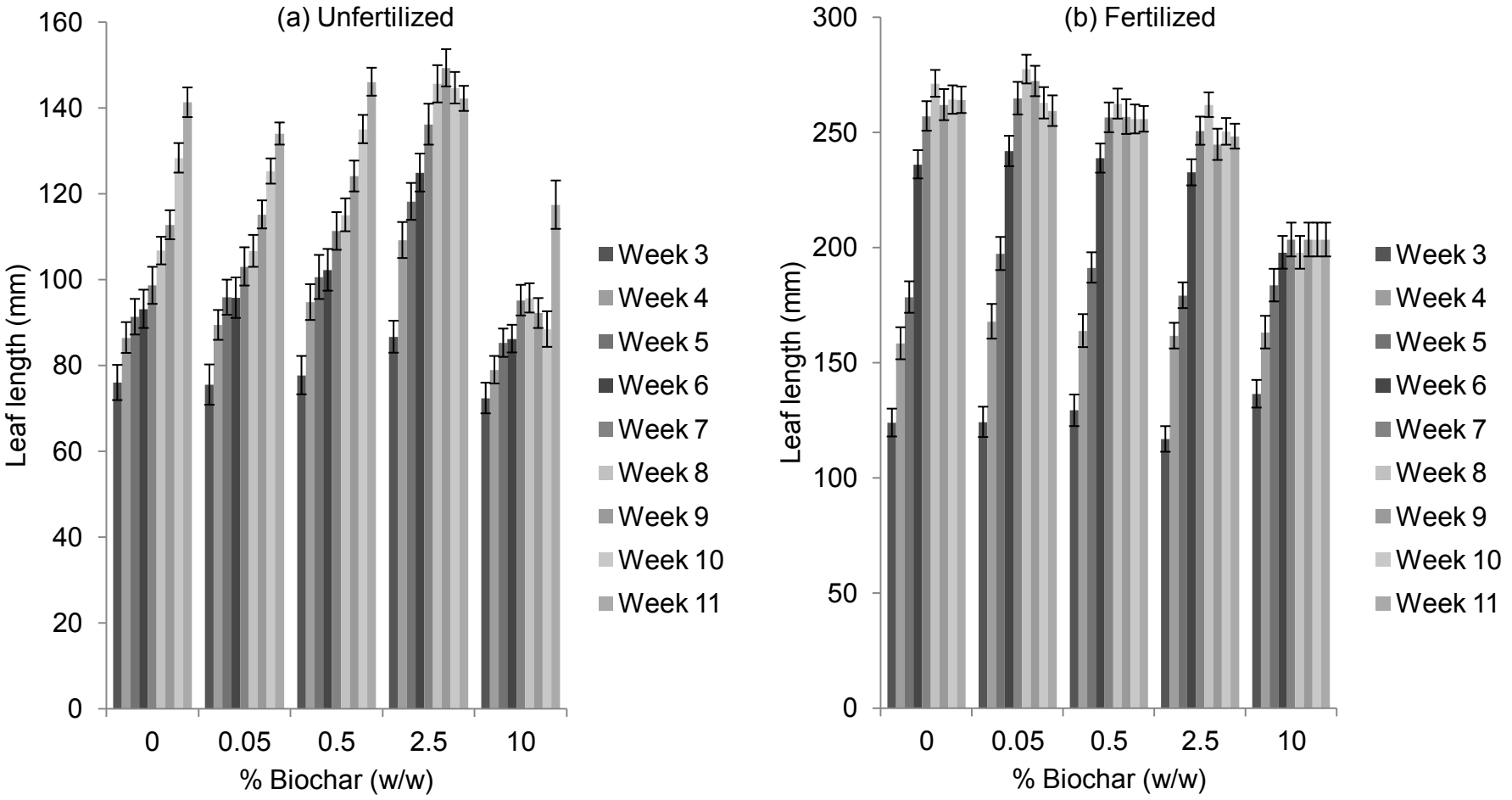


Figure 1.2 Average wheat leaf length growth measurements taken over nine weeks after germination of the (a) unfertilized and (b) fertilized treatments.

Comparisons of the above and below ground biomass of the unfertilized treatments show a significantly higher above ground biomass at the 2.5 % biochar application level (Fig. 1.3a). The fertilized treatments had the highest above ground biomass at the 0.5 % biochar application level (Fig. 1.3b). These results show that the optimum biochar application level for fertilized treatments was 0.5% (Fig. 1.3a), (approximately 10 t ha^{-1} to a depth of 15 cm), while for the unfertilized treatments it was 2.5 %, approximately 50 t ha^{-1} to a depth of 15 cm, (Fig. 1.3b), which resulted in an increase in plant growth of 21 and 29 %, respectively. The below ground biomass of the unfertilized treatments show that the 0.5 % biochar application level had the best root growth with an increase of 20 % growth in comparison to the control treatment (Fig. 1.3a). On the other hand, the fertilized below ground biomass produced the most roots (per mass) at the 0.05 % biochar level (Fig. 1.3b).

Conversely, the wheat pot trial also showed some contrasting yield responses to biochar-amended acidic soils. Although the dry mass production of the fertilized 10 % biochar treatments was higher relative to the unfertilized treatments, stunted growth observed as negative yield responses was evident in both the unfertilized and fertilized treatments (Fig. 1.3). Similar results were reported in the literature whereby studies found yield reductions at higher biochar application levels. It was explained that the substantial increase in soil pH due to the biochar resulted in pH-induced micronutrient deficiencies, and subsequently reduced yields (Kishimoto and Sugiura 1985; Mikan and Abrams 1995).

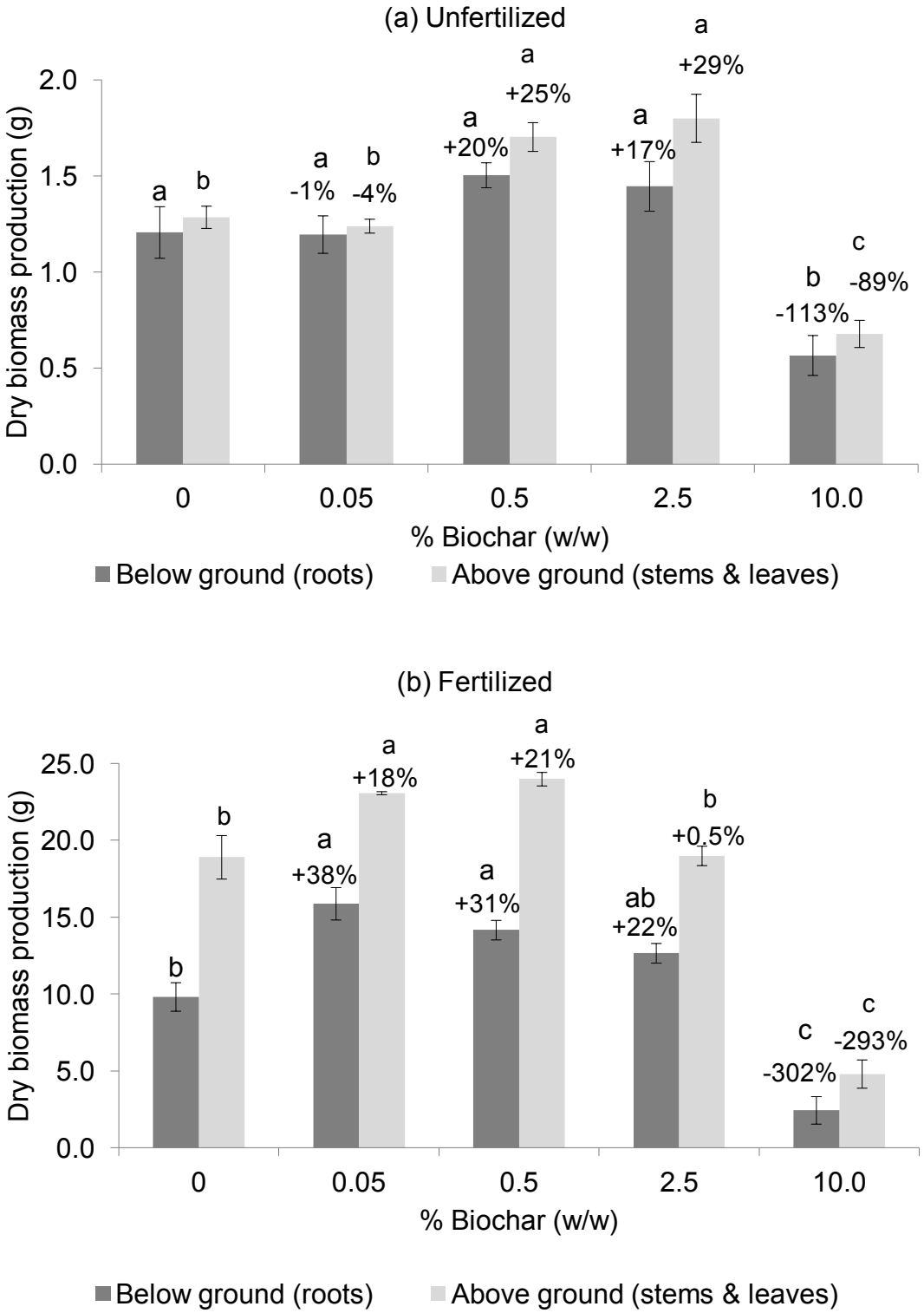


Figure 1.3 Total above and below ground biomass production for (a) unfertilized and (b) fertilized wheat plants showing the relative percentage increase (+) and decrease (-) from the control. All the values for the above and below ground biomass production are significant at the P <0.05 level based on Tukey's Studentized Range test.

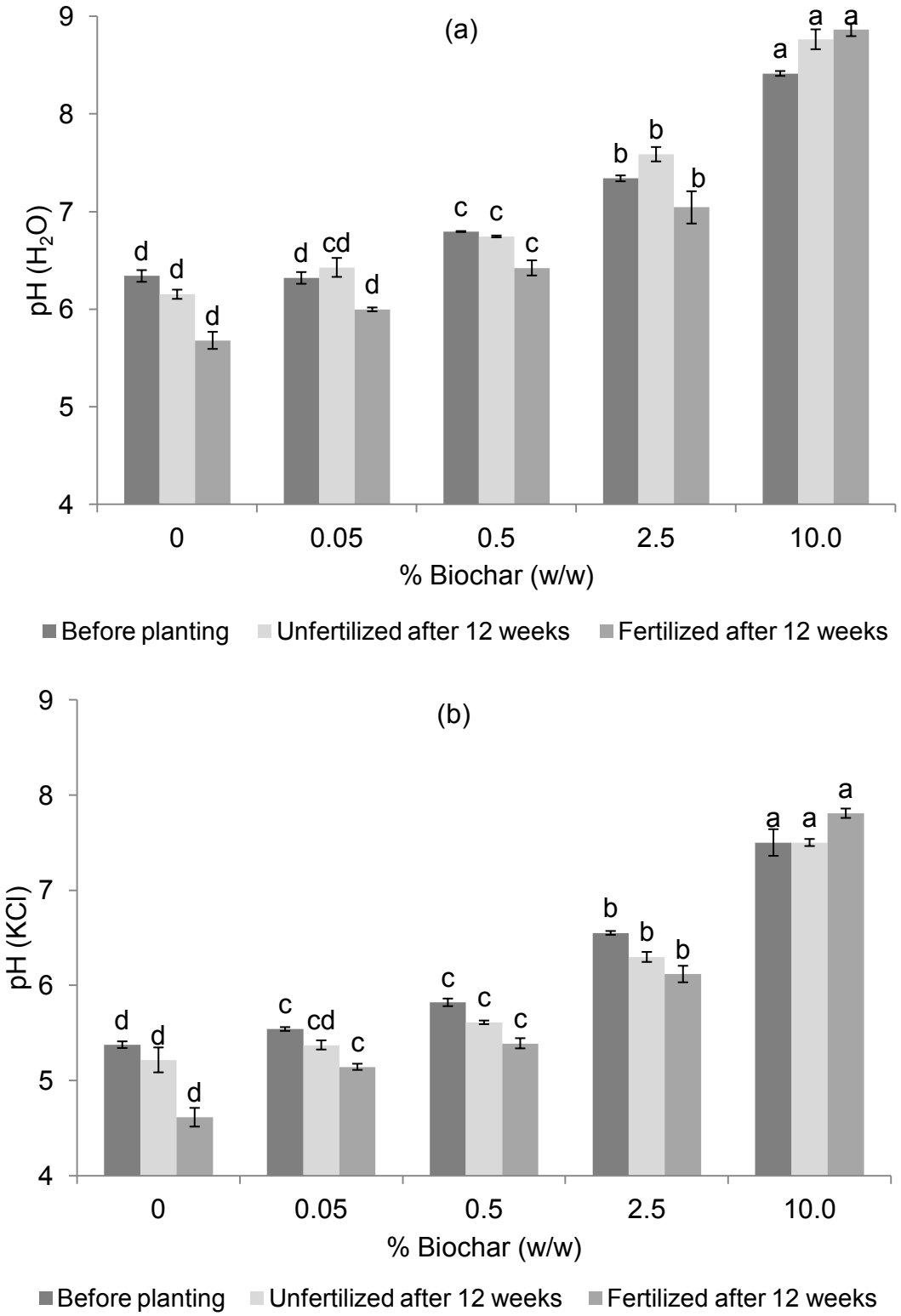


Figure 1.4 Comparison of soil pH changes in both (a) distilled water (H_2O) and (b) 1 M KCl as a result of biochar application at different levels. All of the pH values are significant at the P <0.05 level based on Tukey's Studentized Range test.

3.4.3.2 Effect of biochar on wheat nutrient uptake

Since biochar is produced from organic materials, it inherently contains nutrients that are found in its mineral (or ash) fraction. Therefore, the addition of biochar to soil adds free exchangeable bases such as K, Ca, and Mg to occupy the soil-exchange sites, thus resulting in an increase in soil pH, and readily supplying plant nutrients for growth (Glaser et al. 2002). Our results show that soil pH was partly responsible for the relationships observed in wheat nutrient uptake. A clear trend of significant increase in soil pH with increasing biochar application level to the soil was observed (Fig. 1.4). Similarly, in a study involving an acidic ferrosol, the liming effect of biochar was shown to contribute to soil fertility (Van Zwieten et al. 2010b).

Although the soil-biochar mixtures showed increasing C:N ratios (Table 1.3), it is important to note that the total elemental contents of N, which is organically bound, does not in effect reveal the definite plant available N (Chan and Xu 2009). This is particularly critical since the residual N in the biochar is largely found as recalcitrant heterocyclic N rather than bioavailable amine N (Cao et al. 2009; Novak et al. 2009). The different soil-biochar mixtures had no significant effect on the leaf tissue N content when no fertilizer was applied. Therefore, at the 10 % biochar application level, growth was limited. However, it is likely that the reduced growth was not due to a lack of N uptake as the leaf N content was high (Fig. 1.5).

Reduced uptake of total N in both unfertilized and fertilized treatments was observed particularly when the biochar application level was above 2.5 % (Fig. 1.6). This decrease could possibly be attributed to biological N immobilization, given that the biochar had low N content and high C:N ratio (156:1) (Table 1.3). Similarly, several other studies also found lower N uptake with biochar amendment (Gaskin et al. 2008; Lehmann et al. 2003; Rondon et al. 2007). Therefore, lower N uptake is as a result of the small fraction of biochar that is easily mineralizable, thus consequently leading to N immobilization (Chan and Xu 2009). Furthermore, the difference in leaf N content and total N uptake of the fertilized treatments was possibly due to the size of the overall biomass production of the wheat.

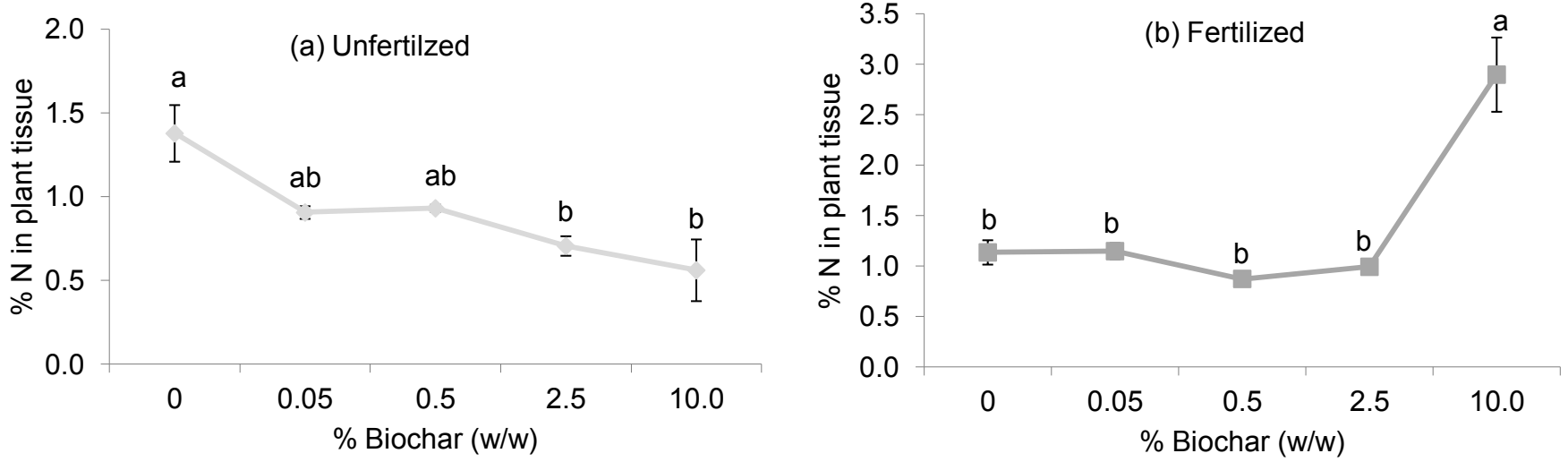


Figure 1.5 Wheat leaf analysis for nitrogen content for the (a) unfertilized and (b) fertilized biochar-amended treatments.

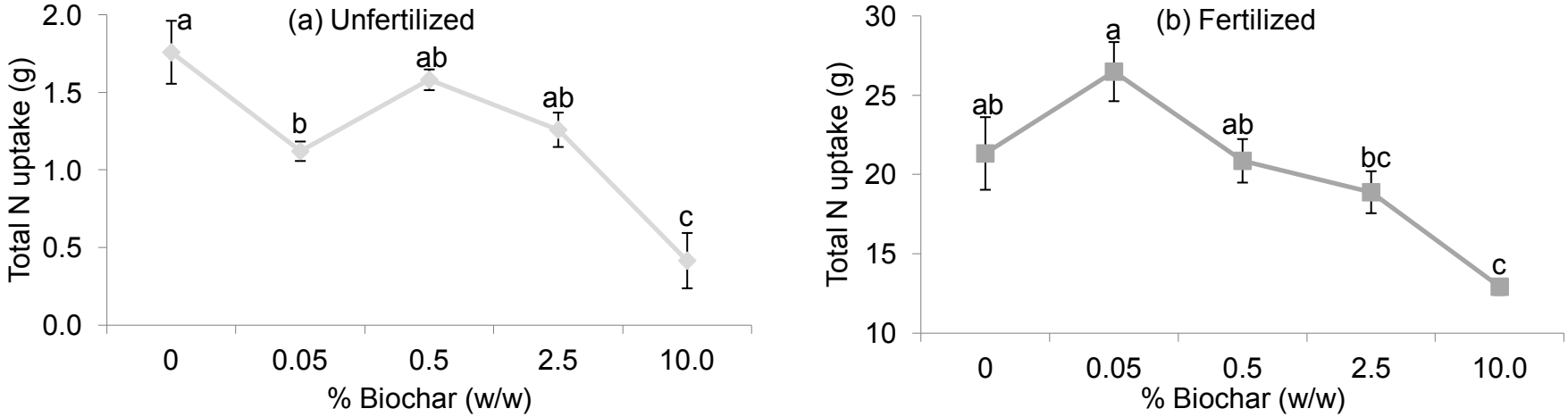


Figure 1.6 Total nitrogen uptake of wheat plants in the (a) unfertilized and (b) fertilized treatments.

Biochar inherently contains a high content of soluble P salts formed during the charring of organic materials (DeLuca et al. 2009). Although the amount of available P found in the biochar is high (Tables 1.7), the soil-biochar mixtures were all below the critical level of 15 ppm (Soltanpour and Follett 1991), thus suggesting a P deficiency. Given that P has its plant availability largely affected by pH-dependent abiotic reactions, and biochar having variable P availability by either providing anion exchange capacity, or by influencing the activity of Al, Fe and Ca ions (DeLuca et al. 2009), could explain the insufficient plant available P in the soil-biochar mixtures. The dissimilarities observed in the total leaf content and uptake of P in the unfertilized and fertilized treatments provide likely evidence to this.

In the unfertilized treatment (Fig. 1.7a), the P wheat leaf content initially accumulated significantly until the 2.5 % level, and then declined; whereas in the fertilized treatment, an intense rise in wheat leaf P content was observed between the 2.5 and 10.0 % levels (Fig. 1.7b). In addition, P uptake of the unfertilized treatment increased and reached the highest uptake at the optimal biochar application level of 2.5 % (Fig. 1.8a). The subtle pH changes between the control soil, no biochar added, and biochar-amended soils, suggest considerably less P precipitation with Al^{3+} and Fe^{3+} (DeLuca et al. 2009) which resulted in higher soluble P, and thus greater P uptake in the unfertilized treatments (Fig. 1.8a). In contrast, a decrease in total P uptake of the fertilized treatments was observed possibly due to the effect of the broad spectrum fertilizer (Fig. 1.8b).

While it is common for excessive amounts of one nutrient to induce excessive accumulations of another nutrient, the opposite is also valid (Taiz and Zeiger 2002). Therefore, nutrient deficiencies or the over-accumulation of nutrients may result in inhibited plant growth. This interpretation supports the observation of stunted growth at the 10.0 % unfertilized and fertilized treatments (Fig. 1.3). Thus it is suggested that the high P tissue content is likely responsible for the decline in plant growth at the 10.0 % treatments (Fig. 1.7).

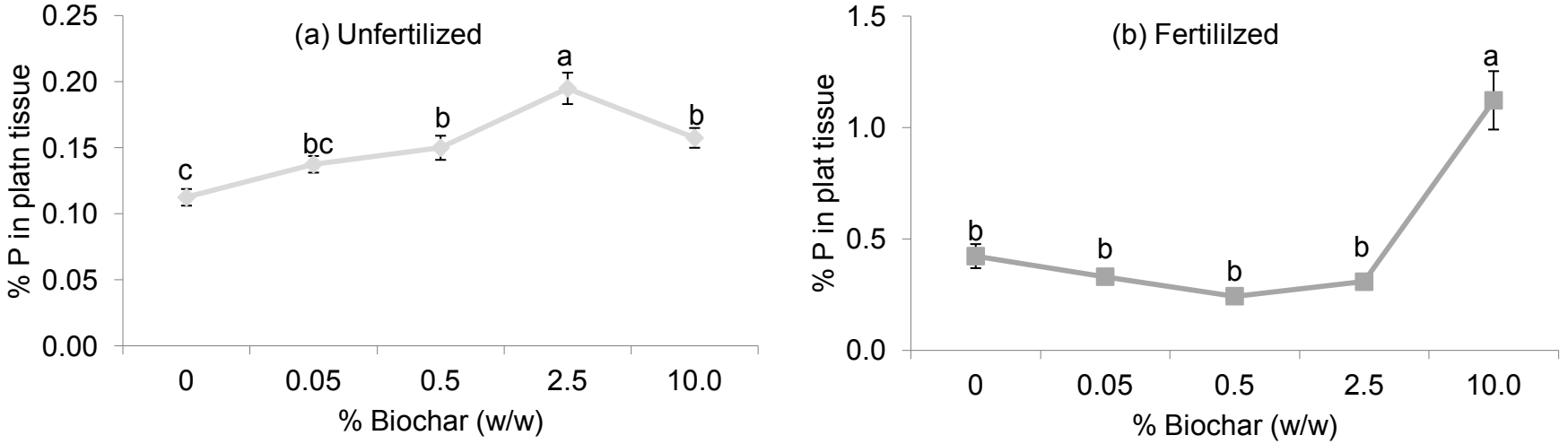


Figure 1.7 Wheat leaf analysis for phosphorus content in the (a) unfertilized and (b) fertilized biochar-amended treatments.

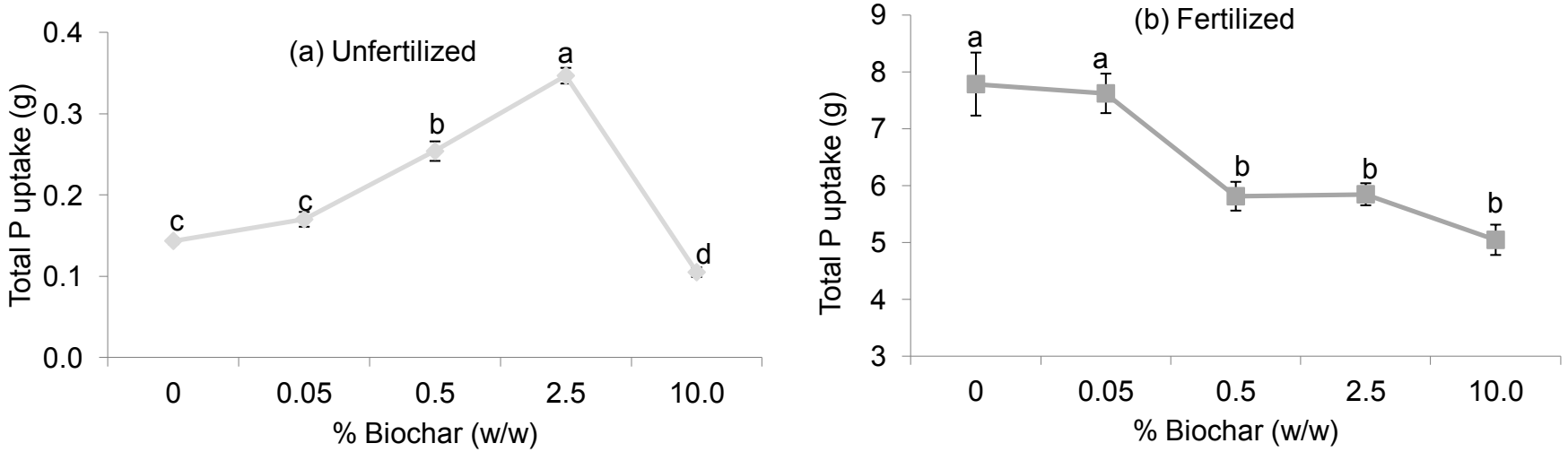


Figure 1.8 Total phosphorus uptake of wheat plants in the (a) unfertilized and (b) fertilized treatments.

The pine biochar used in this study inherently contains significant amounts of K (Tables 1.5, 1.6 and 1.9), with the exchangeable K considered as being optimal at the critical level of 0.2 $cmol_c kg^{-1}$ (van der Linde et al. 2007). These results correspond with the increase in AB-DTPA plant available K at increasing levels of biochar application (Table 1.7). However, this increase did not exceed the critical value of 180 ppm for plant available K (Soltanpour and Follett (1991). Figure 1.9 shows that both the unfertilized and fertilized treatments had little variation in wheat leaf content of K between the control and 2.5 %, and as expected, a greater accumulation at the 10.0 level.

On the other hand, K uptake of the fertilized treatments shows that the highest total uptake was at the 2.5 % biochar application level (Fig. 1.10.b). Figure 1.11 illustrates that there was a strong direct correlation with an increase in the unfertilized total uptake treatments and the total above ground biomass. Therefore, the greater the K availability which resulted in greater K uptake of the unfertilized wheat plants most likely resulted in greater above ground biomass production.

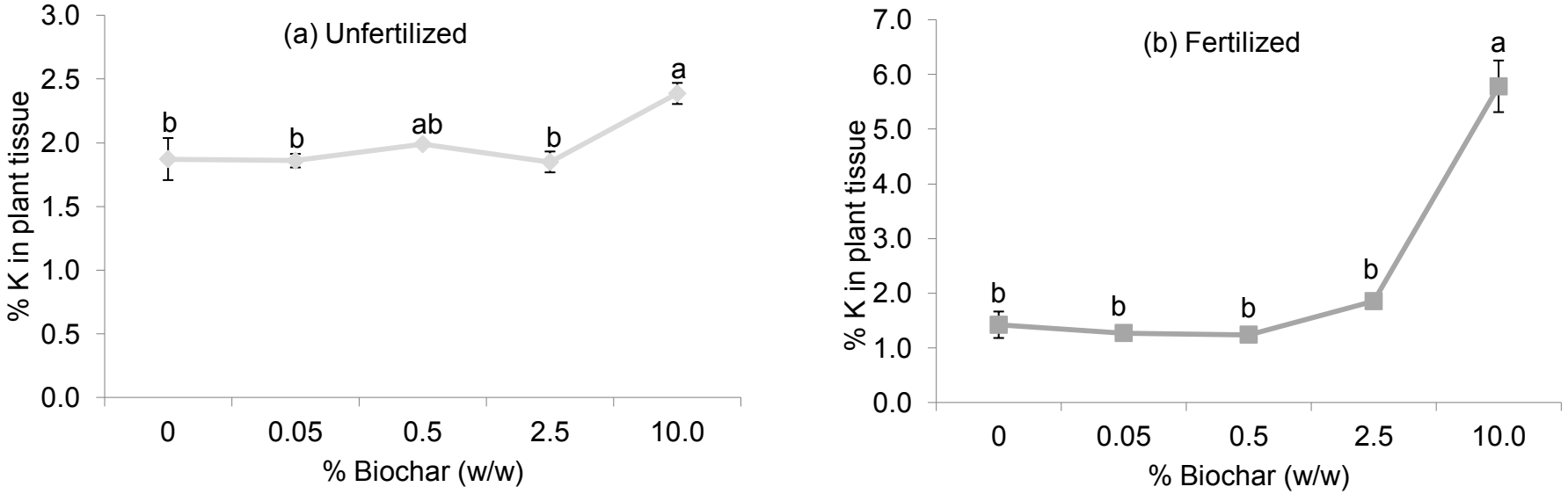


Figure 1.9 Wheat leaf analysis for potassium content in the (a) unfertilized and (b) fertilized biochar-amended treatments.

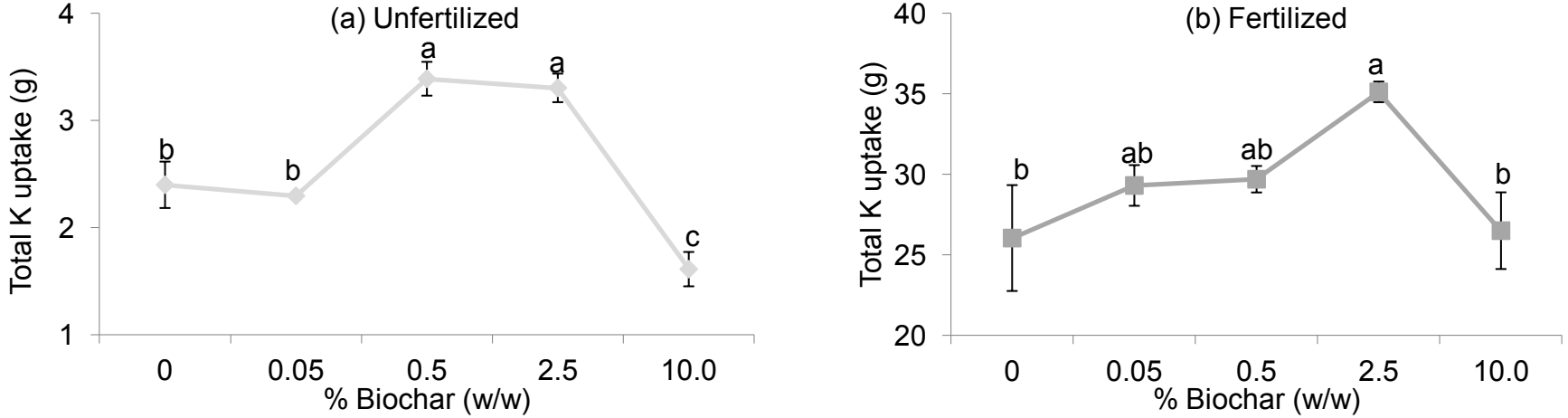


Figure 1.10 Total potassium uptake of wheat plants in the (a) unfertilized and (b) fertilized treatments.

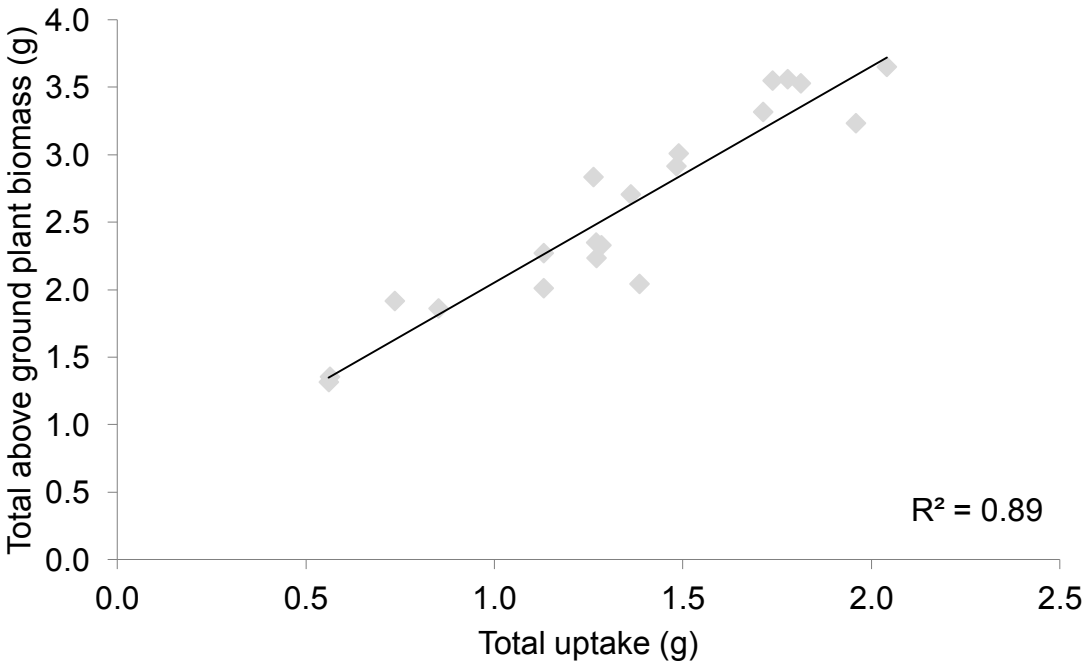


Figure 1.11 Direct correlation of total potassium uptake vs. total above ground biomass yield of the unfertilized treatments.

The uptake of calcium and magnesium decreased in fertilized treatments when the biochar level was above 0.05 % (Figs. 1.13 and 1.15). It is likely that the uptake of Ca was limited in the unfertilized and fertilized treatments at the 2.5 and 10.0% due to Ca-carbonate ($CaCO_3$) or Ca-phosphate ($CaPO_4$) precipitation because of the high pH.

The fertilized sulfur (S) wheat leaf content was the highest at the 10.0 % level (Fig. 1.16), however, a steady decrease in total uptake was observed with increasing biochar application (Fig. 1.17). This is possibly due to the increasing N deficiency of all the treatments with increasing biochar application, as N deficiency may inevitably result in a decrease in N assimilation (Havlin et al. 2005; Salvagiotti et al. 2009). Fertilization with both N and S has been found to have a major synergistic effect. Benefits have been observed when increases in the amount of N fertilizer added resulted in improved vegetative tissue, grain yield and N uptake (Salvagiotti et al. 2009).

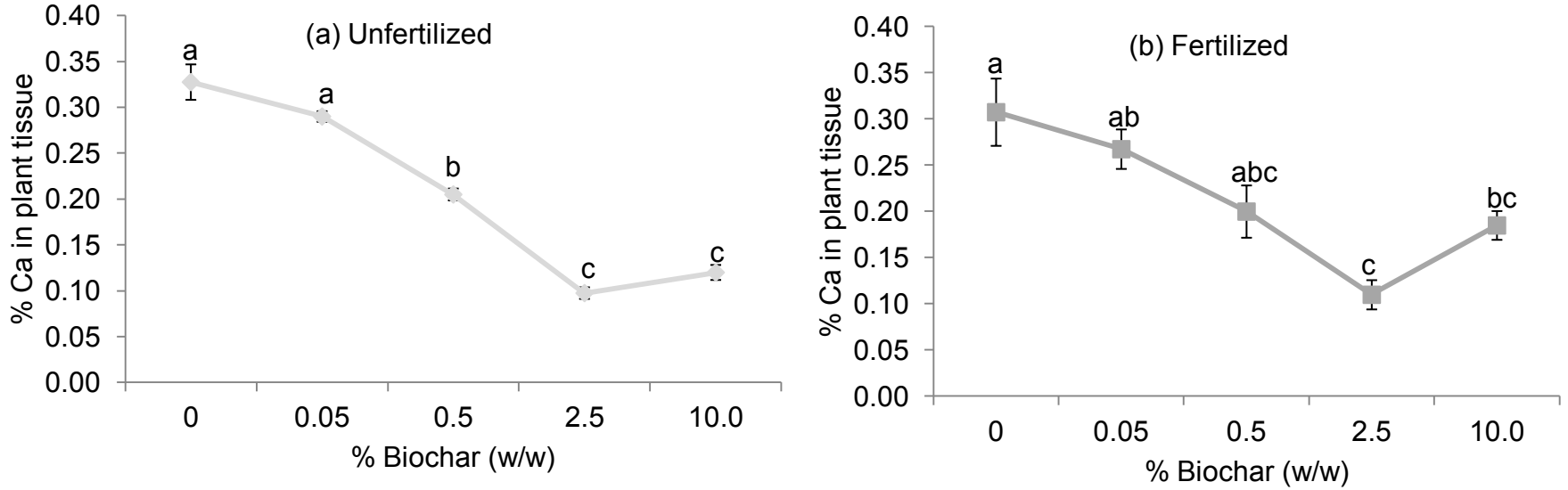


Figure 1.12 Wheat leaf analysis for calcium content in the (a) unfertilized and (b) fertilized biochar-amended treatments.

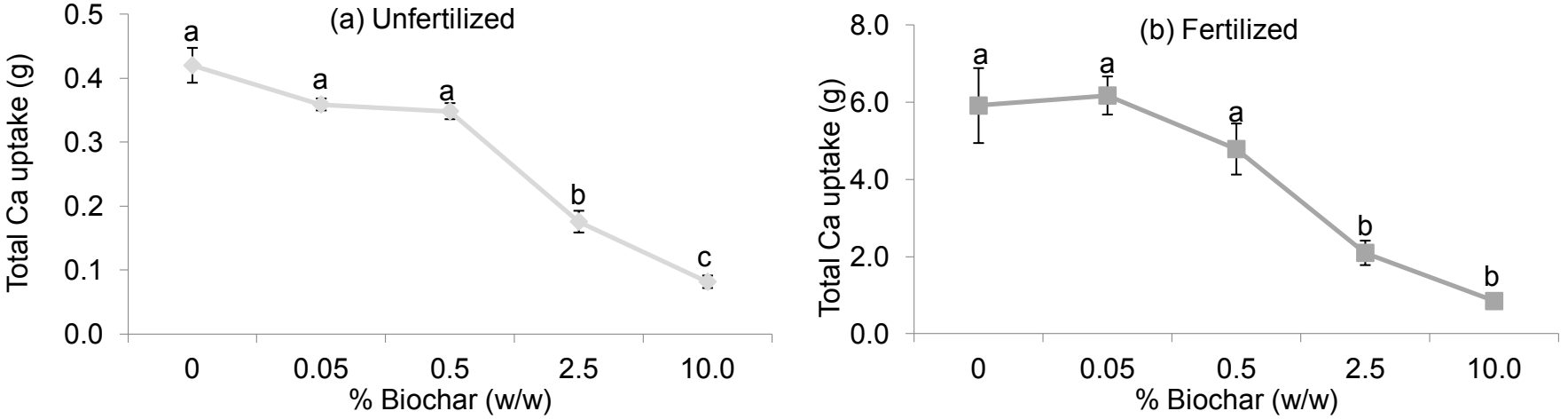


Figure 1.13 Total calcium uptake of wheat plants in the (a) unfertilized and (b) fertilized treatments.

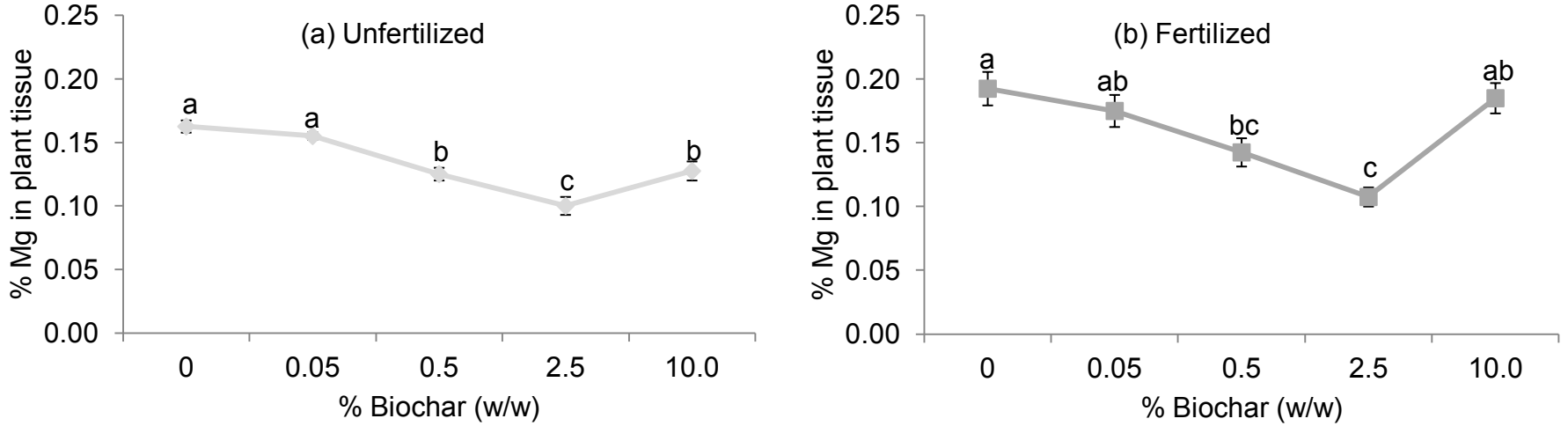


Figure 1.14 Wheat leaf analysis for magnesium content in the (a) unfertilized and (b) fertilized biochar-amended treatments.

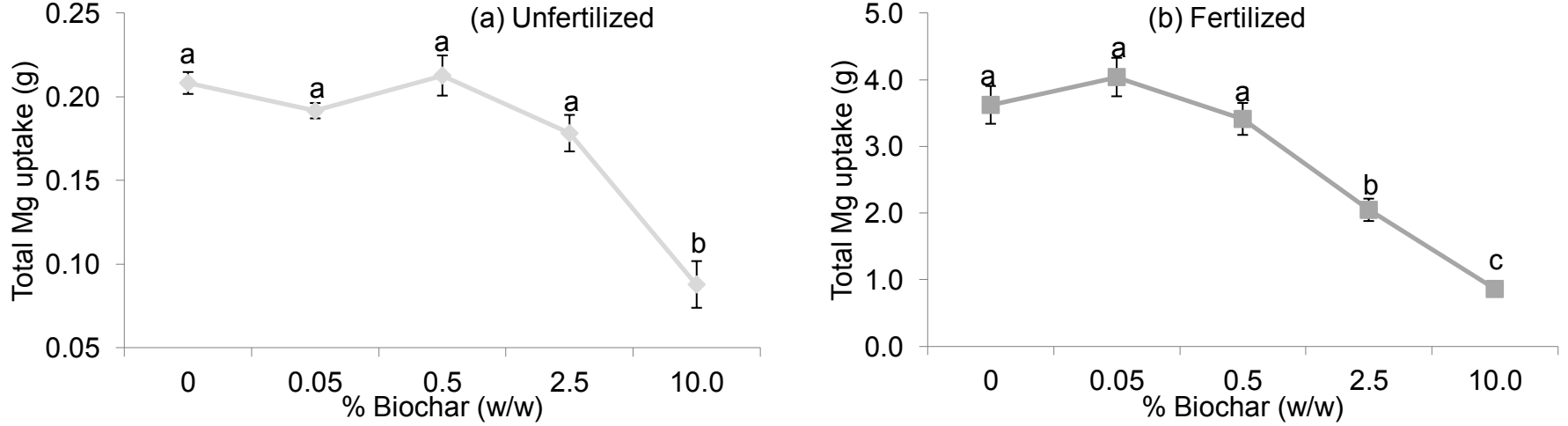


Figure 1.15 Total magnesium uptake of wheat plants in the (a) unfertilized and (b) fertilized treatments.

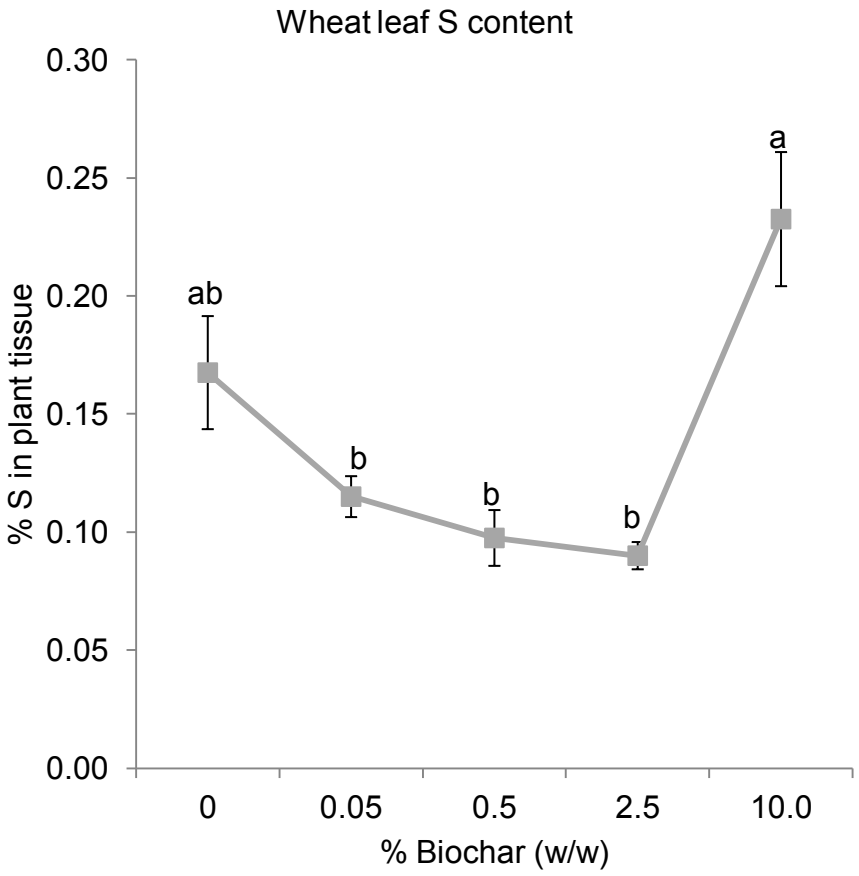


Figure 1.16 Wheat leaf analysis of sulfur in the fertilized biochar treatments.

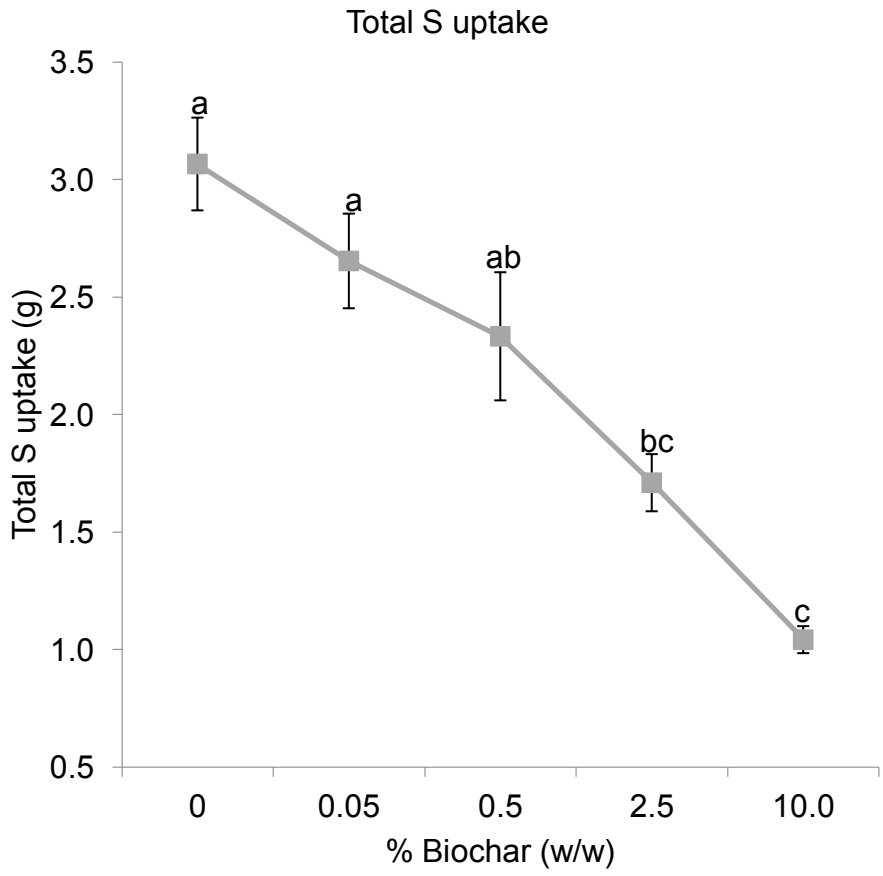


Figure 1.17 Total sulfur uptake of wheat plants in the fertilized treatments.

Although aluminium is a non-essential element, it is a mineral constituent found in soil and biochar (Amonette and Joseph 2009) (Table 1.8). Acidic soils in particular, usually have toxic Al^{3+} levels associated with P deficiencies, which greatly limit plant growth (Clark 1977). Considering that 40 % of global arable soil is acidic, P deficiency is often reported in combination with Al toxicity (Ligaba et al. 2004). This reasoning likely implies that the relatively high P tissue content (Fig. 1.7a) and increased P uptake of the unfertilized treatments (Fig. 1.8a) up to the 2.5 % biochar application levels, are due to reduced Al toxicity.

Aluminium wheat tissue content of the fertilized 10.0 % treatment (Fig. 1.18) shows the highest Al concentration. In contrast, a sharp reduction in both the unfertilized and fertilized 10.0 % wheat Al uptake is observed (Fig. 1.19). This observation is due to the solubility of Al and the range in pH values of the soil and soil-biochar mixtures. This interpretation is supported by the likely soil chemistry mechanisms that resulted in this nutrient adaptation. The binding of phosphate anions ($H_2PO_2^-$) to soil particles bearing Al or Fe cations may result in an exchange with phosphate due to negatively charged hydroxyl groups (OH^-). In turn, because phosphate may be tightly bound, and relatively less mobile, this mechanism results in limited P availability, which inevitably limits plant growth (Taiz and Zeiger 2002). The application of biochar to highly weathered soils has been reported to show an immediate yield response when there is a reduction in soil pH and Al toxicity (Blackwell et al. 2009). This response is primarily induced by the carbonates in biochar which facilitate the alleviation of the toxic effects of exchangeable Al in acidic soils (Chan and Xu 2009). Furthermore, Al is a polyvalent cation that competes for binding sites in the apoplasm and consequently results in reducing the uptake of Ca, Mg, Mn and Zn (Miyasaka et al. 2007).

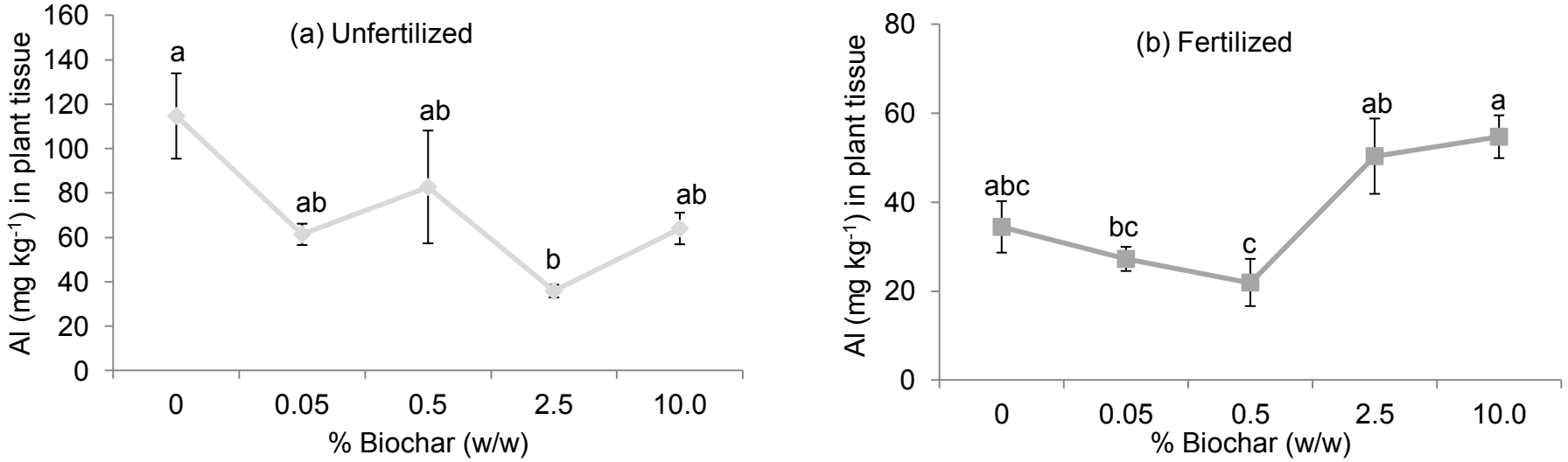


Figure 1.18 Wheat leaf analysis for aluminium content of the (a) unfertilized and (b) fertilized biochar-amended treatments.

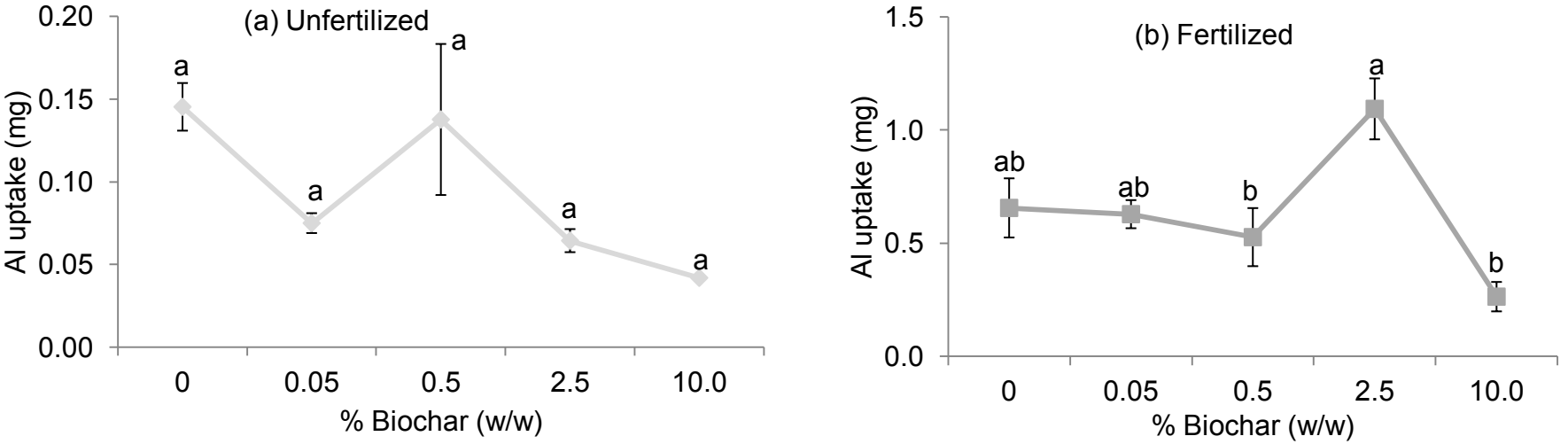


Figure 1.19 Total aluminium uptake of wheat plant in the (a) unfertilized and (b) fertilized biochar-amended treatments.

The essential micronutrients iron, manganese and copper are generally less available in soil solution in the root system because their ions are increasingly adsorbed on soil particles with increasing soil pH (Taiz and Zeiger 2002). The AB-DTPA plant availability test shows that Fe was sufficient at all levels of biochar amendment and at the control (Table 1.7). Accordingly, the wheat plant tissue shows that the Fe concentration in the tissue is above the critical value of 25 mg kg^{-1} (dry weight) (Fig. 1.20). In contrast, Figure 1.21 shows that the uptake of Fe generally decreased in both the unfertilized and fertilized treatments. This is because the addition of biochar to soil results in the precipitation of Fe, making it physically unavailable to the plant, and thereby lowering the mobility of Fe into phloem cells for long distance translocation (Taiz and Zeiger 2002). However, since Fe is affected by soil pH, primarily found as oxides and hydroxides in soil solution, and is chelated by organic matter (Pais and Jones 1997), it is likely that biochar enables cations such as Ca to form soluble complexes that are more physically available to the plant (Taiz and Zeiger 2002).

Although plant available manganese is deficient in the soil (Table 1.7), the wheat leaf content is above the critical level of 30 mg kg^{-1} for all unfertilized treatments except the 10.0 % biochar application level (Fig. 1.22a). In contrast, the wheat leaf content is below the critical level for the biochar-amended fertilized treatments (Fig. 1.22b). A particularly high efficiency in the uptake of Mn was observed at both the unfertilized and fertilized 2.5 % biochar (w/w) application levels (Fig. 1.15). This suggests high soil solution Mn^{2+} at the 2.5 % level which may play an essential role in photosynthesis (Havlin et al. 2005), which particularly manifested in growth benefits at the unfertilized 2.5 % biochar level (Fig. 1.3b). Furthermore, Mn uptake for both unfertilized and fertilized treatments declined between the 2.5 and 10.0 % treatments (Fig. 1.23). This is expected as Mn deficiency is related to a high pH above 7.5, and increasing soil organic matter content (Pais and Jones 1997).

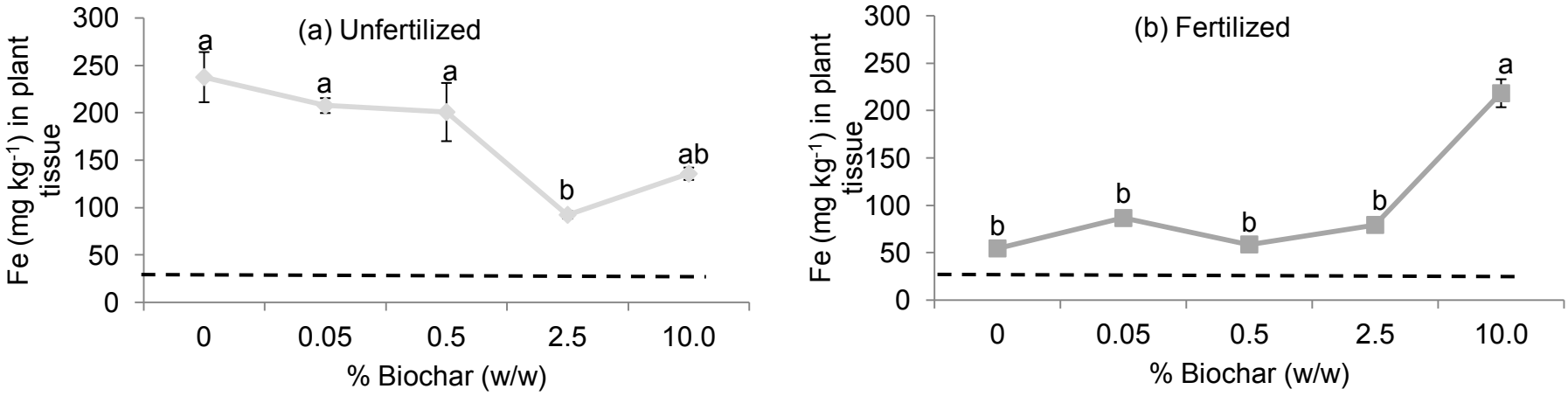


Figure 1.20 Wheat leaf analysis for iron content in the (a) unfertilized and (b) fertilized biochar-amended treatments. The critical value of Fe is 25 mg kg^{-1} (van der linde et al. 2007).

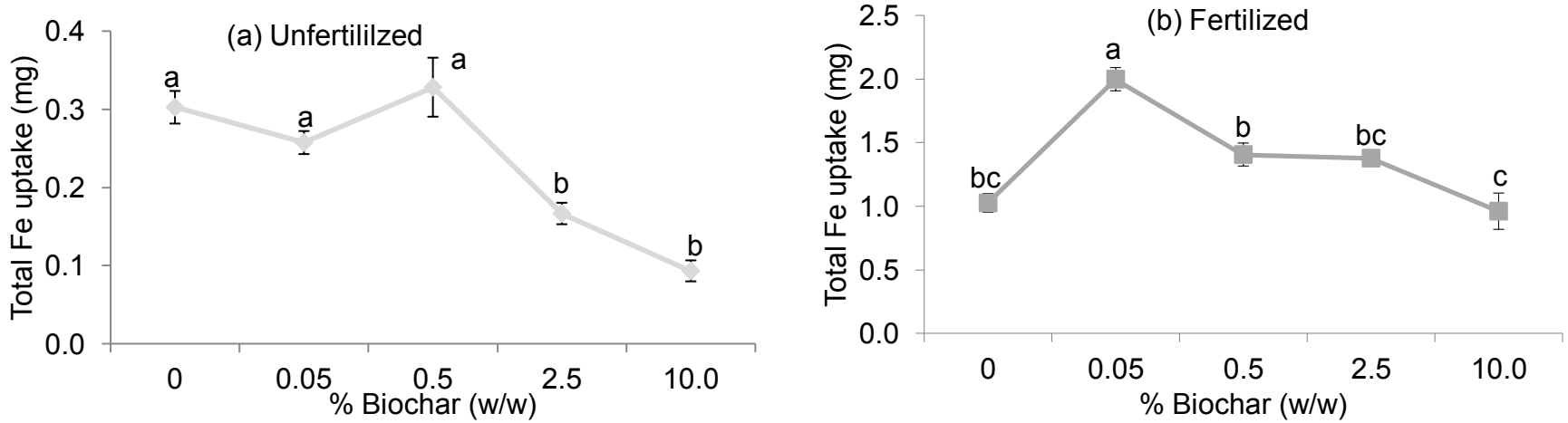


Figure 1.21 Total iron uptake of wheat plant in the (a) unfertilized and (b) fertilized biochar-amended treatments.

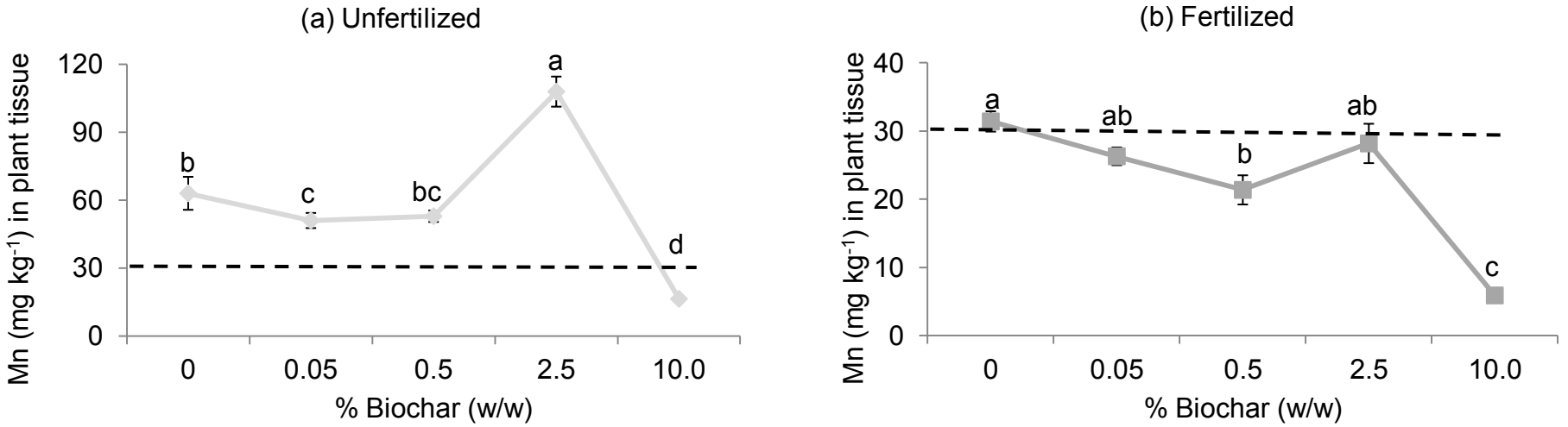


Figure 1.22 Wheat leaf analysis for manganese content in the (a) unfertilized and (b) fertilized biochar-amended treatments. The critical value of Mn is 30 mg kg^{-1} (van der linde et al. 2007).

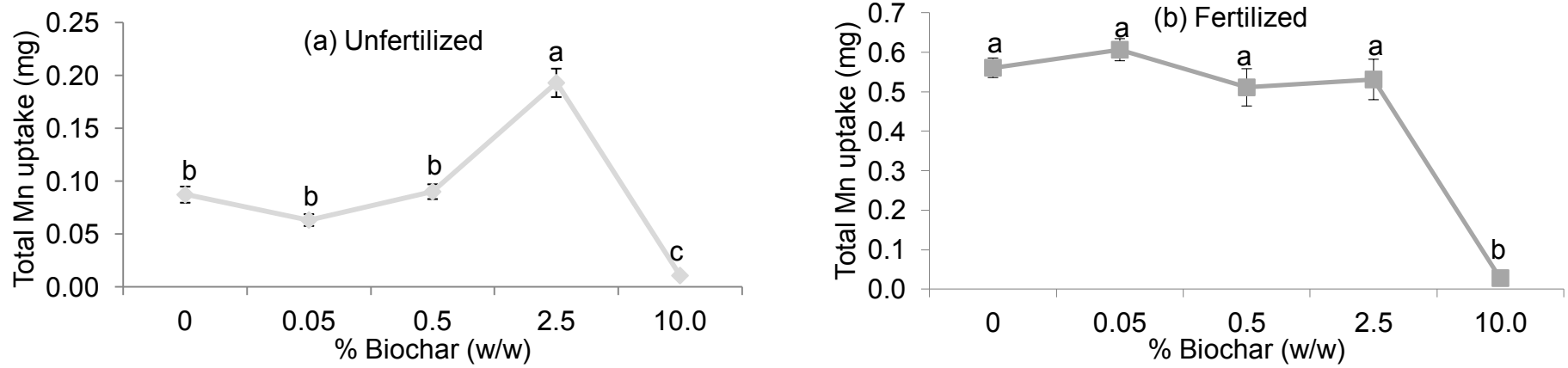


Figure 1.23 Total manganese uptake of wheat plant in the (a) unfertilized and (b) fertilized biochar-amended treatments.

The soil and soil-biochar mixtures were all deficient in plant available copper as they were below the critical AB-DTPA level of 2.0 mg kg^{-1} (Table 1.7). However, the leaf content of the unfertilized treatments gave evidence that the biochar provided some Cu as the content was above the 5.0 mg kg^{-1} critical level (Fig. 1.24a). In spite of this sufficiency, the 2.5 and 10.0 % biochar application levels showed a decline in the wheat leaf content. This suggests that the soil-biochar interactions at these levels caused the suppression of the uptake of Cu. This interpretation is confirmed by the cascading effect observed in the unfertilized total plant uptake of Cu (Fig. 1.25a).

In contrast, the fertilized treatments show that although the fertilizer aids in increasing the Cu wheat leaf concentration, it was only at the 10.0 % that the leaf norm was met (Fig. 1.24b). Furthermore, the plant uptake of Cu in the unfertilized and fertilized treatments decreased with an increase in biochar application (Fig. 1.25). It is suggested that the decline in Cu plant availability may be attributed to factors such as the liming of soil by biochar, the influence of added phosphates from the fertilizer, and the addition of organic matter (Pais and Jones 1997).

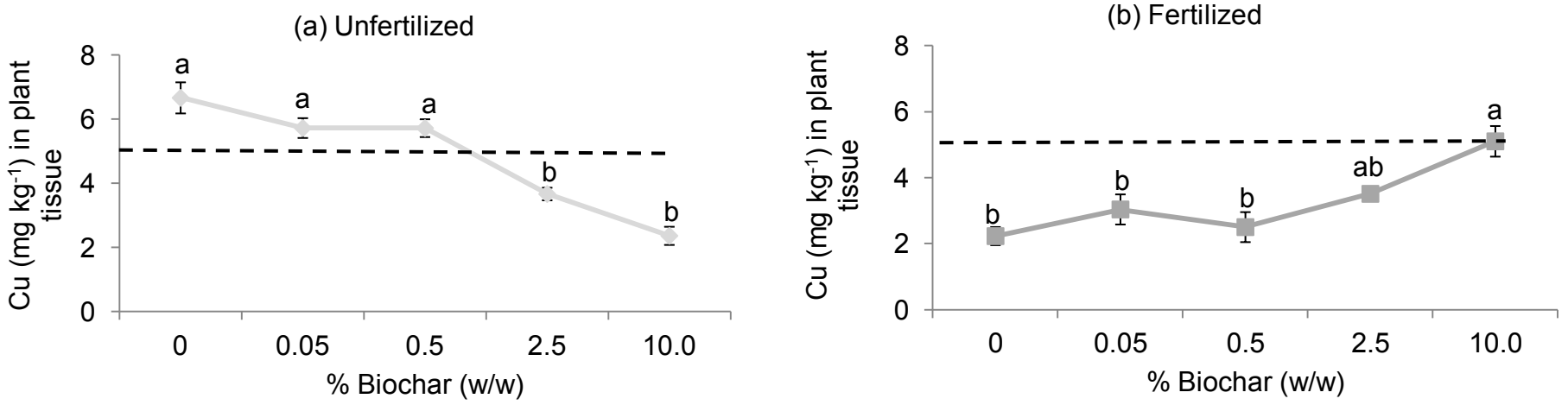


Figure 1.24 Wheat leaf analysis for copper content in the (a) unfertilized and (b) fertilized biochar-amended treatments. The critical value of Cu is 5 mg kg^{-1} (van der linde et al. 2007).

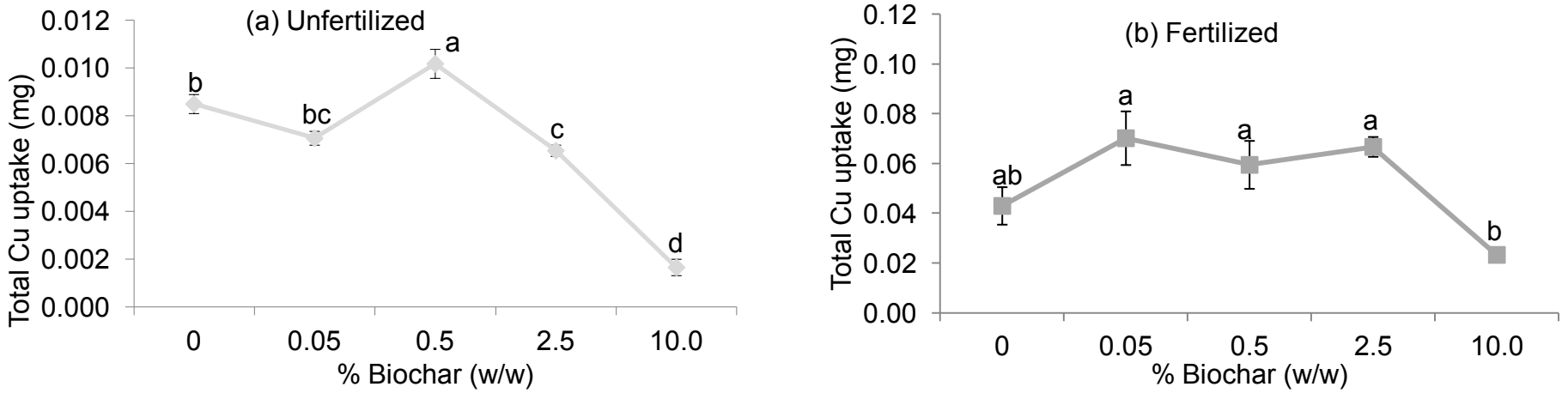


Figure 1.25 Total copper uptake of wheat plant in the (a) unfertilized and (b) fertilized biochar-amended treatments.

Table 1.7 also shows that plant available zinc was mostly deficient except at the 0.05 and 10.0 % biochar application levels. However, biochar seems to have provided an accumulation of Zn as the wheat leaf content of the unfertilized treatments were sufficient above 15 mg kg^{-1} at the 10.0 % biochar application level (Fig. 1.26). In contrast, the fertilized treatments were sufficient at all levels. Since Zn deficiency predominantly manifests in leached sandy soils low in organic matter, with neutral to alkaline pH values (Pais and Jones 1997), it was expected that the soil-biochar system indicated a decrease in Zn uptake (Fig. 1.27). Although monocotyledons such as wheat generally require lower B (1-6 mg kg^{-1}) concentrations than dicotyledons (20-70 mg kg^{-1}) (Pais and Jones 1997), both unfertilized and fertilized treatments of the wheat leaf analysis were deficient across all levels of biochar application (Fig. 1.26).

Comparisons of B and Zn showed that the wheat tissue content of the unfertilized treatments of B and Zn decreased with an increase in the addition of biochar (Figs. 1.26 and 1.28). In addition, these micronutrients were suppressed during wheat plant uptake (Figs. 1.27 and 1.29). This demonstrates that the biochar has a high sorption capacity for B and Zn. This suppression of B and Zn uptake was attributed to an increase in soil pH with increasing amounts of biochar, as pH affects speciation. Boron becomes less available, while Zn and other trace metals can be precipitated out at higher pH values. As a result, excessive liming of acid soils induces a considerable reduction in the Zn content of plants (Armour and Brennan 1999). Generally, a Zn deficiency may occur under cold and wet conditions. Zinc availability is further affected by high available P (Table 1.7), other nutrient deficiencies, and prolonged waterlogging (Armour and Brennan 1999).

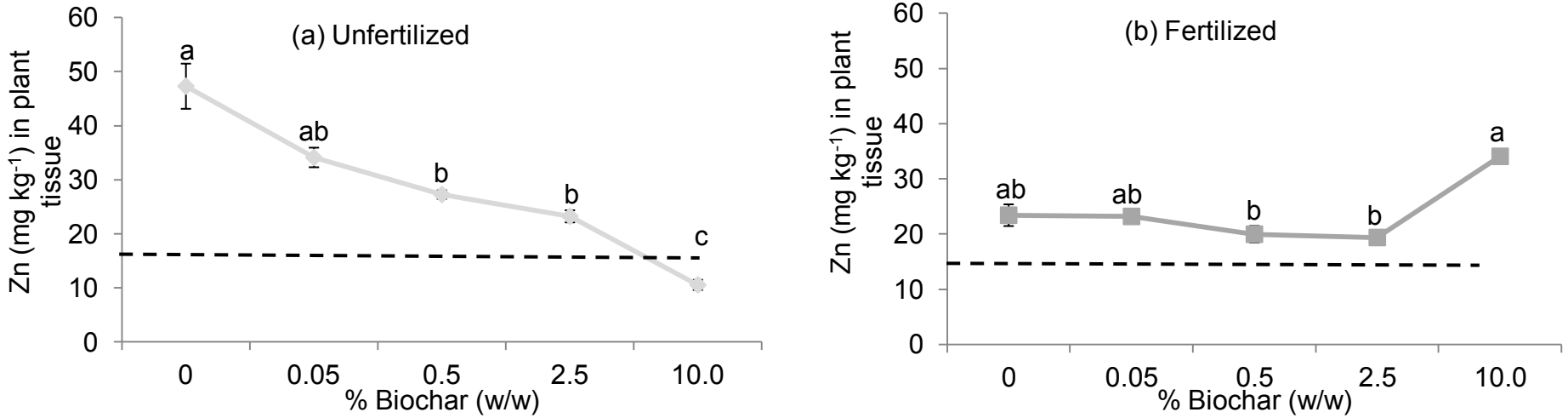


Figure 1.26 Wheat leaf analysis for zinc content in the (a) unfertilized and (b) fertilized biochar-amended treatments. The critical value of Zn is 15 mg kg^{-1} (van der linde et al. 2007).

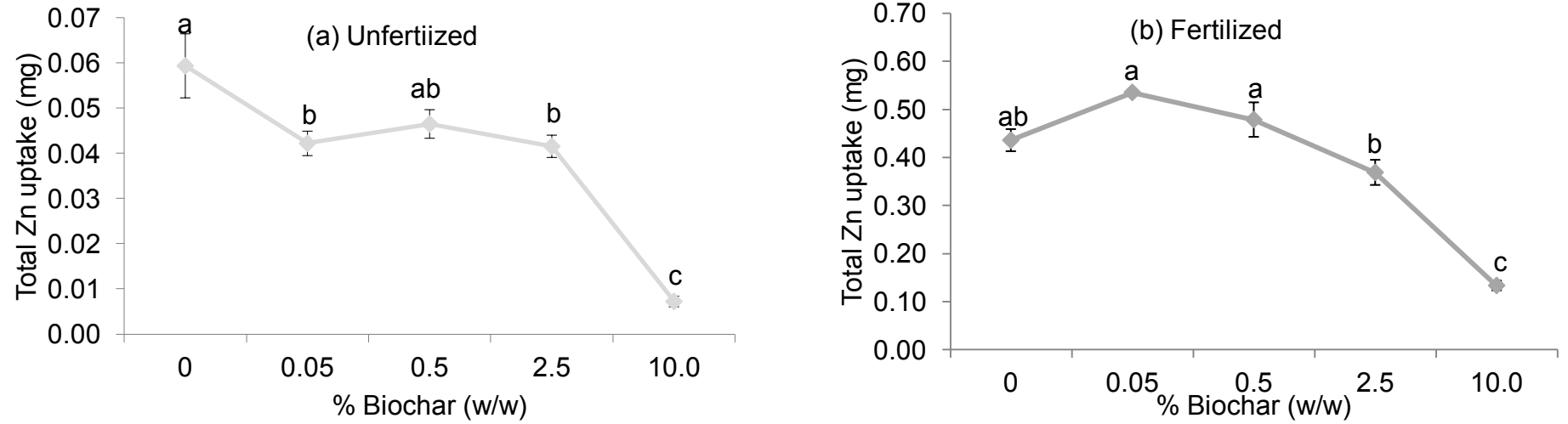


Figure 1.27 Total zinc uptake of wheat plant in the (a) unfertilized and (b) fertilized biochar-amended treatments.

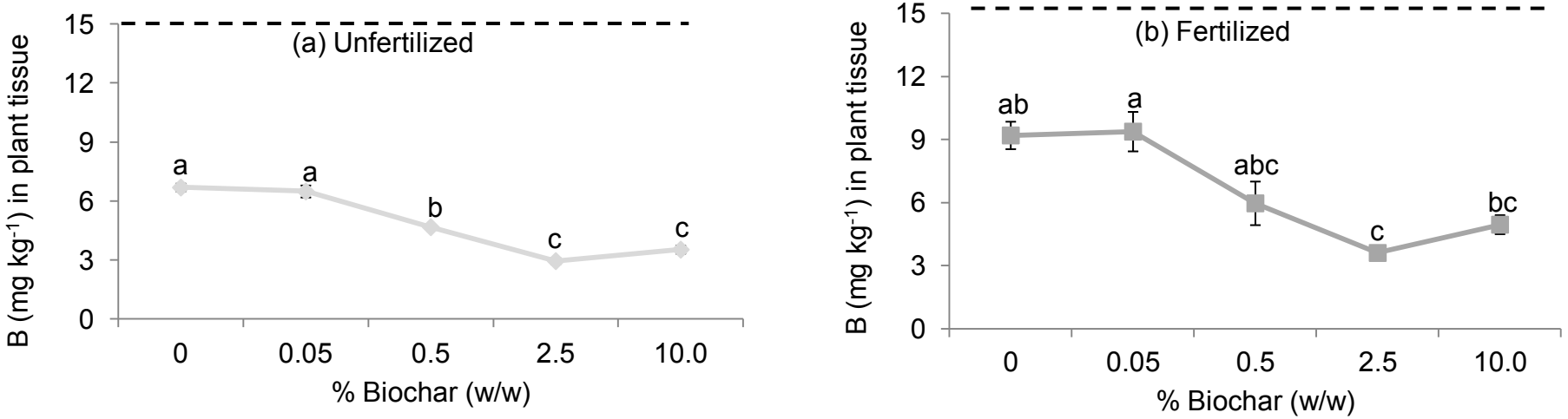


Figure 1.28 Wheat leaf analysis for boron content in the (a) unfertilized and (b) fertilized biochar-amended treatments. The critical value of B is 15 mg kg^{-1} (van der linde et al. 2007).

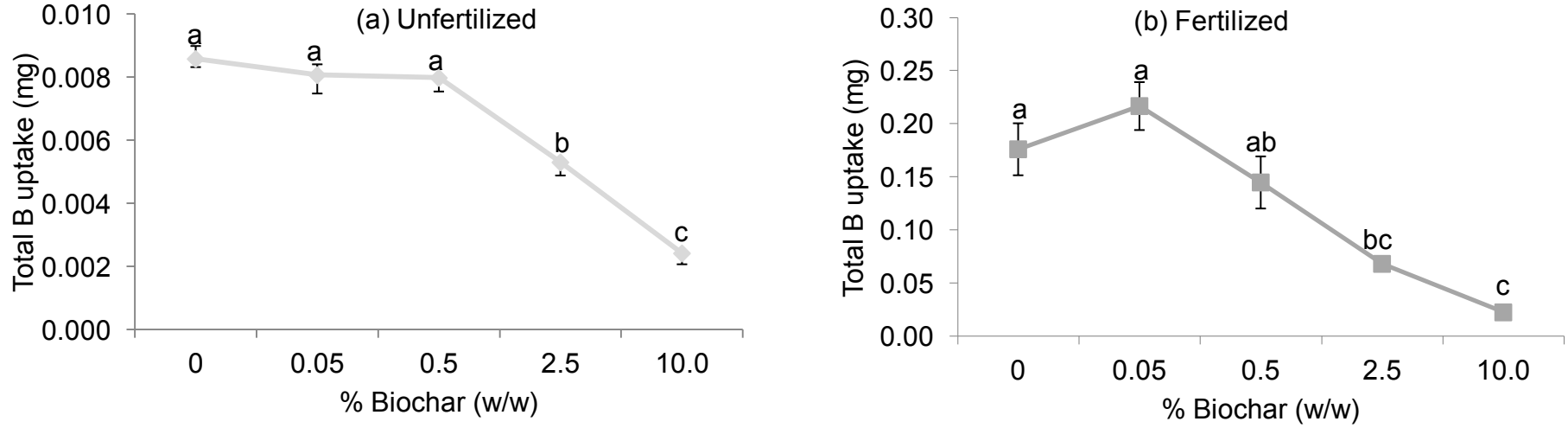


Figure 1.29 Total boron uptake of wheat plant in the (a) unfertilized and (b) fertilized biochar-amended treatments.

The results from the current study show that low biochar application levels between 0.05 and 2.5 % (w/w) generally show a significant increase in plant growth. This was evident based on the increase in soil pH, increase in the availability of basic cations, and improved wheat biomass production. The increase in wheat tissue content and/or uptake of the fertilized treatments in P, K, Fe, Zn and Cu provides evidence for good biochar-fertilizer interaction. These results were similar to studies conducted by Van Zwieten et al. (2010b). The low uptake efficiency of the micronutrients Fe and Cu suggest that they may prevent toxicity accumulations when biochar is added without fertilizer. Despite the many benefits of biochar amendment to sandy soil, the high 2.5 and 10.0 % (w/w) biochar application rate, approximately 50 and 200 t ha^{-1} to a depth of 15 cm, was inappropriate for use in agricultural practice. Similarly, Glaser et al. (2002) found that charcoal additions above 100 t ha^{-1} led to negative responses.

3.4.3.3 Effect of biochar on wheat roots

Biochar amendment of the acidic sandy soil showed interesting below ground biomass differences between 0.05 and 0.5 % biochar compared to the control. The investment in root growth and the allocation of resources to roots was a major factor to emphasize nutrient acquisition and consequently higher plant growth at the fertilized 0.05 and 0.5 % biochar application levels (Fig. 1.3b). The unfertilized 0.05 % biochar application level seems to have enhanced the root resource availability of the wheat (Fig. 1.30). This can be attributed to the wheat crop increasing its root biomass in order to take advantage of the increased availability of nutrient resources and moisture in the biochar in comparison to the control. Further evidence of the latter is seen at the 0.05 % level where the Zn and Fe plant available nutrients are the highest in comparison to all of the treatments (Table 1.7).

On the contrary, any percentage biochar beyond this application level reduced root growth. At the fertilized 2.5 % biochar, the root investment was higher than the control (Fig. 1.31). However, this did not translate into higher growth of plant mass. The reason could be that biochar affected the physical (structural) properties of the soil system (Downie et al. 2009) by increasing the bulk density, inhibiting root growth, and thus, by extension reducing nutrient uptake subsequently and plant growth (Fageria and Moreira 2011).

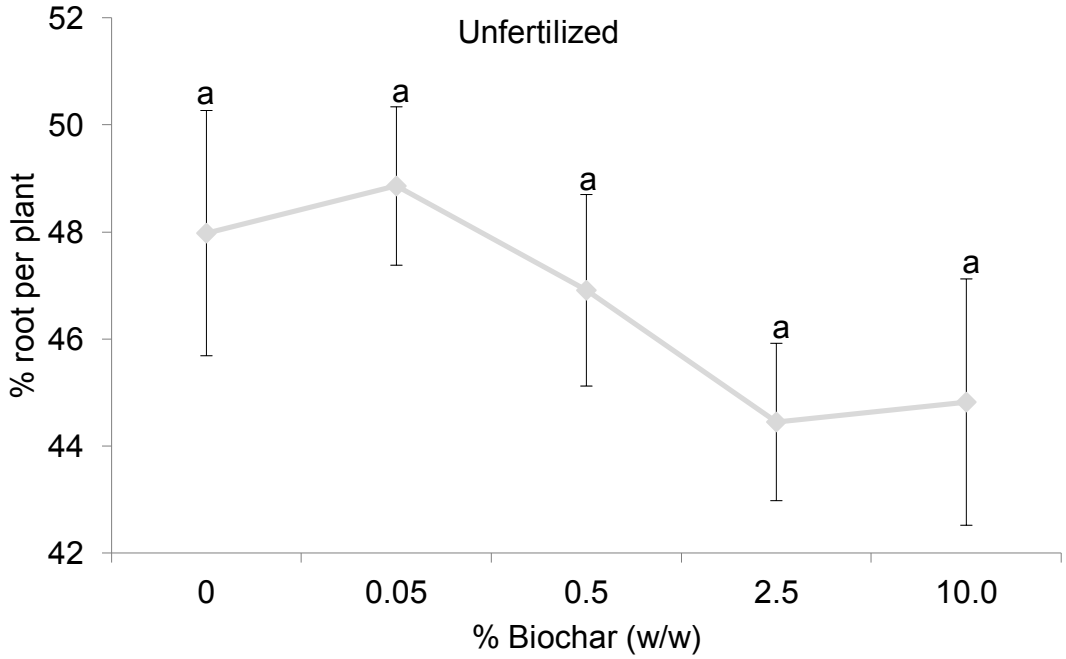


Figure 1. 30 Percentage average root per plant of the unfertilized wheat treatments.

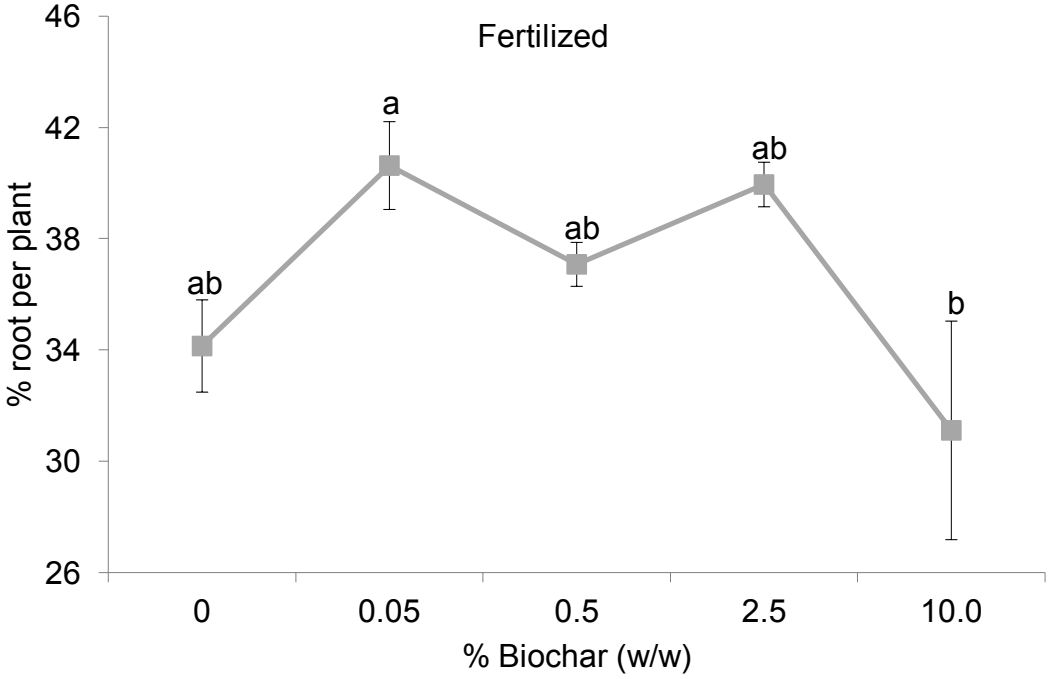


Figure 1.31 Percentage average root per plant (above and below ground) of the fertilized wheat treatments.

3.4.3.4 Effect of biochar on wheat leaves

With increasing biochar application levels, there was an increase in the shoot:root ratio in the unfertililzed treatments (Fig. 1.32a). This suggests that biochar was directly affecting the distribution of assimilates to plant organs to favour a greater shoot production relative to roots. The highest shoot:root ratio was reached at the 2.5 % biochar (w/w) application level, and remained relatively unaffected at the 10.0 % biochar (w/w) level. This plant physiological relation concurs with the 2.5 % biochar application level in the absence of fertilizer achieving the optimal above ground biomass (Fig. 1.3a). Further, this may imply that 2.5 % biochar is the minimum threshold for plant function involving biochar additions in the absence of fertilizer.

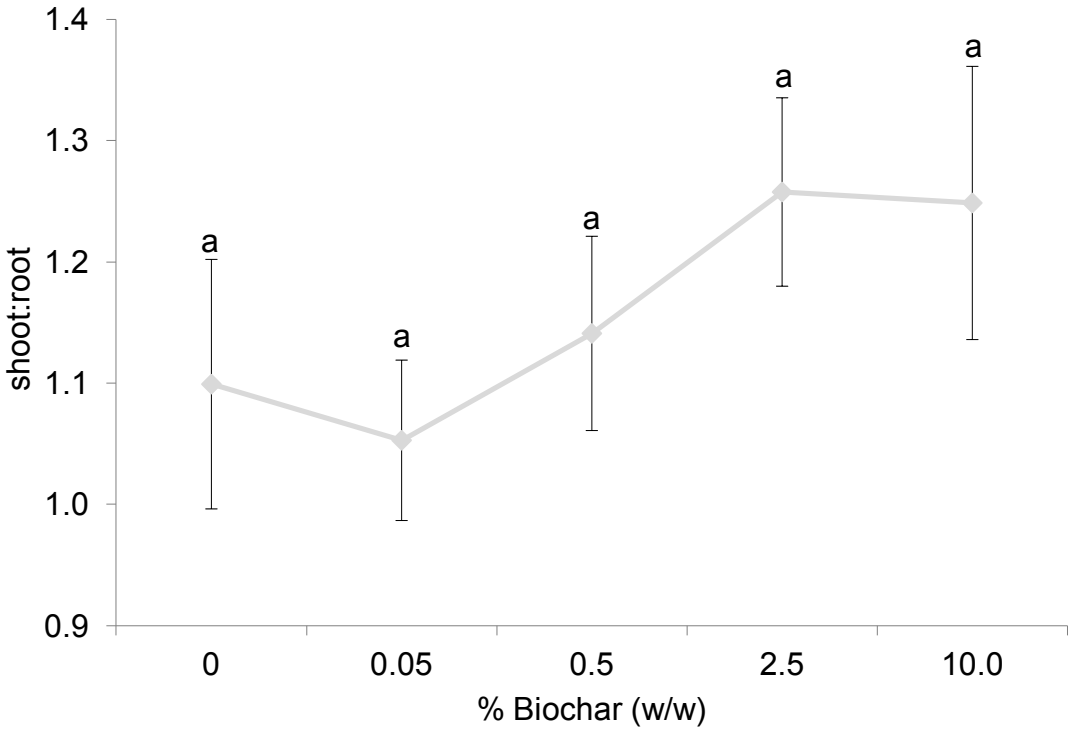


Figure 1.32 Differences in the shoot:root ratio of the unfertilized wheat treatments at different biochar application levels.

With this shift towards relative shoot production with increasing biochar application levels in the absence of fertilizer, there was also an increase in the specific leaf area (SLA) (Fig. 1.33). Cornelissen et al. (2003) described SLA as an indication of a positive direct relationship of the potential relative growth rate expressed as its oven-dry mass of the one-sided area of a fresh leaf. A small SLA is characterized by a

long leaf lifespan, whereby a large SLA is normally found where there is an abundance of nutrients. Incidentally, the increasing SLA at the unfertilized treatments (Fig. 1.33) corresponds with the N (Fig. 1.6) and P (Fig. 1.7) plant tissue contents. The difference in SLA of the fertilized treatments did not differ significantly. This may imply that P may have influenced the reduced availability of nutrient uptake for leaf growth and above ground biomass production (Rodriguez et al. 1998).

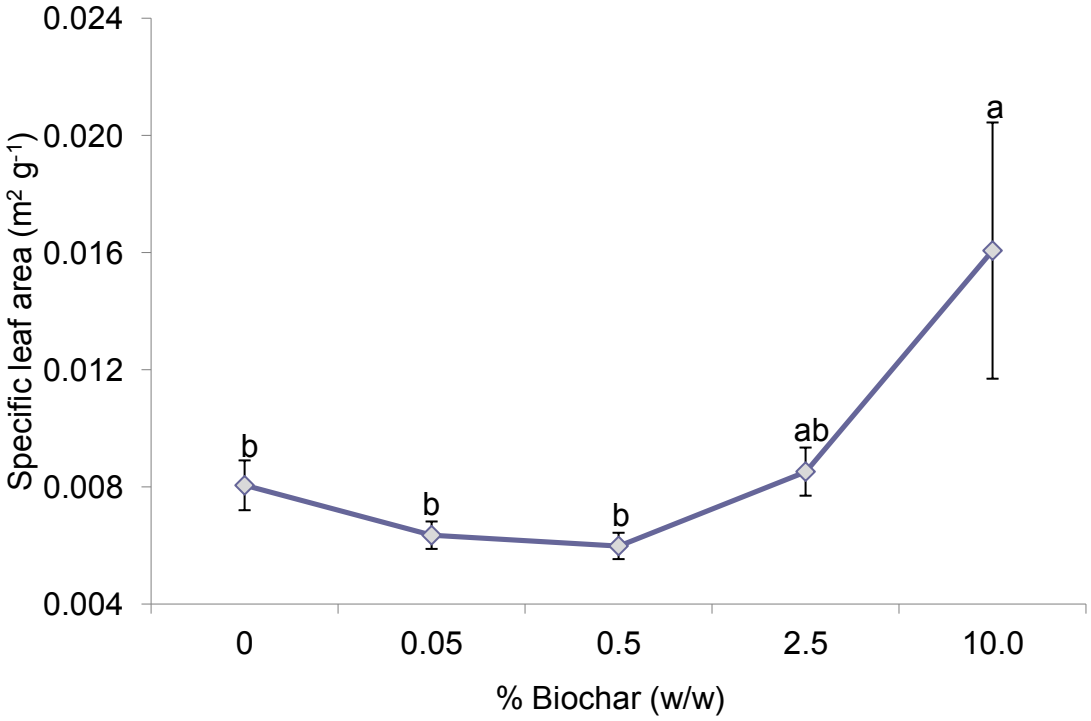


Figure 1.33 Specific leaf area of the unfertilized wheat leaves.

3.4.4 Wheat pot trial harvested at maturity

It took 22 weeks for the wheat plants to reach maturity. The optimum biochar application level for both above- and below ground biomass production was observed at 0.5 %, approximately 10 t ha^{-1} to a depth of 15 cm. This resulted in an increase of 15 and 27 % of above- and below ground biomass respectively (Fig. 1.34). In addition, the 0.5 % biochar application level had a greater overall investment in below ground biomass than the control (Fig. 1.34), while the 2.5% level compared similarly with an increase of 21 % in below ground biomass. Furthermore, the average wheat grain mass harvested at the 0.5 % level was the highest (Fig.1.35), with 6 % more grain mass than the control.

Overall, the mature wheat pot trial did not perform as expected due to the fact that a N deficiency developed and was corrected too late. A nitrogen deficiency in wheat restricts grain yield as a consequence of the reduction in available N when soil N mineralization is not enough to fulfil the crop demand, thereby suggesting that grain yield will increase when N fertilizer is supplied (Salvagiotti et al. 2009). Therefore, it is suggested that in future, wheat grown in biochar-amended sandy soils should be closely monitored for N deficiency symptoms. In addition, the application of N fertilizer should be spread out throughout the crop growing season to ensure that plants do not initially grow vigorously, and then later have all the soil N depleted. To promote a cation-anion balance within the plant (Bloom 1994), it is suggested that the additional N is applied as a balanced mixture of cations (NH_4^+) and anions (NO_3^-) to ensure that the possible immediate increase in soil pH, frequently noticed with an exclusive nitrate application is reduced (Asher and Edwards 1983).

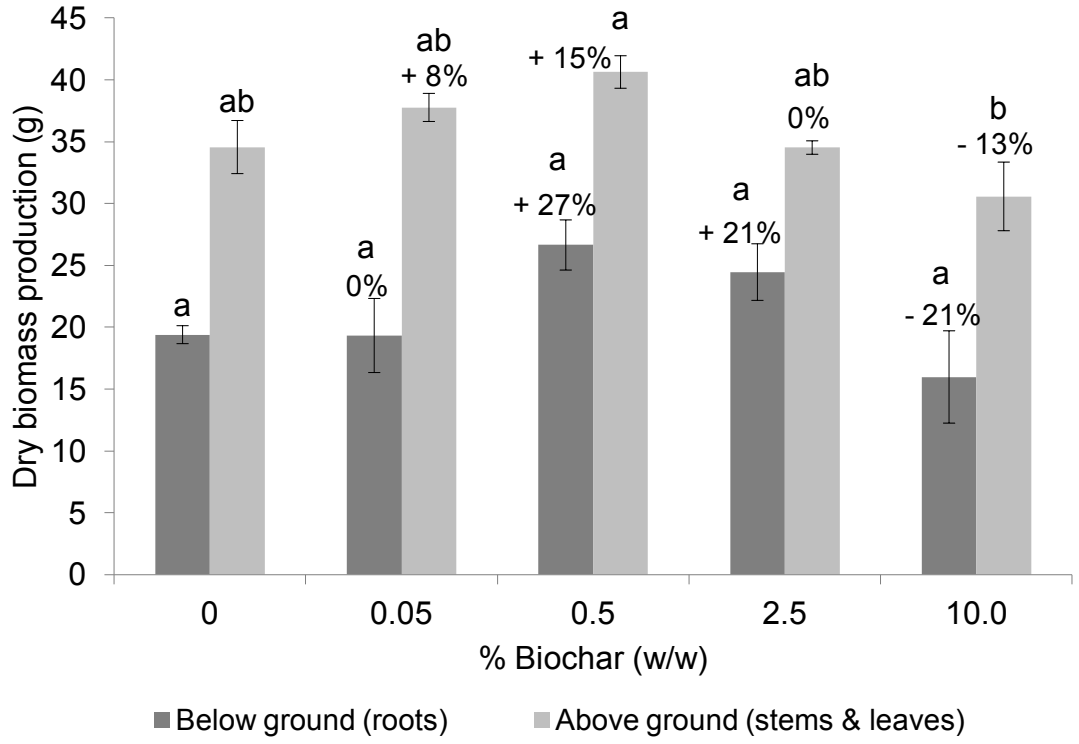


Figure 1.34 Total above- and below ground biomass yield of fertilized wheat plants harvested at maturity.

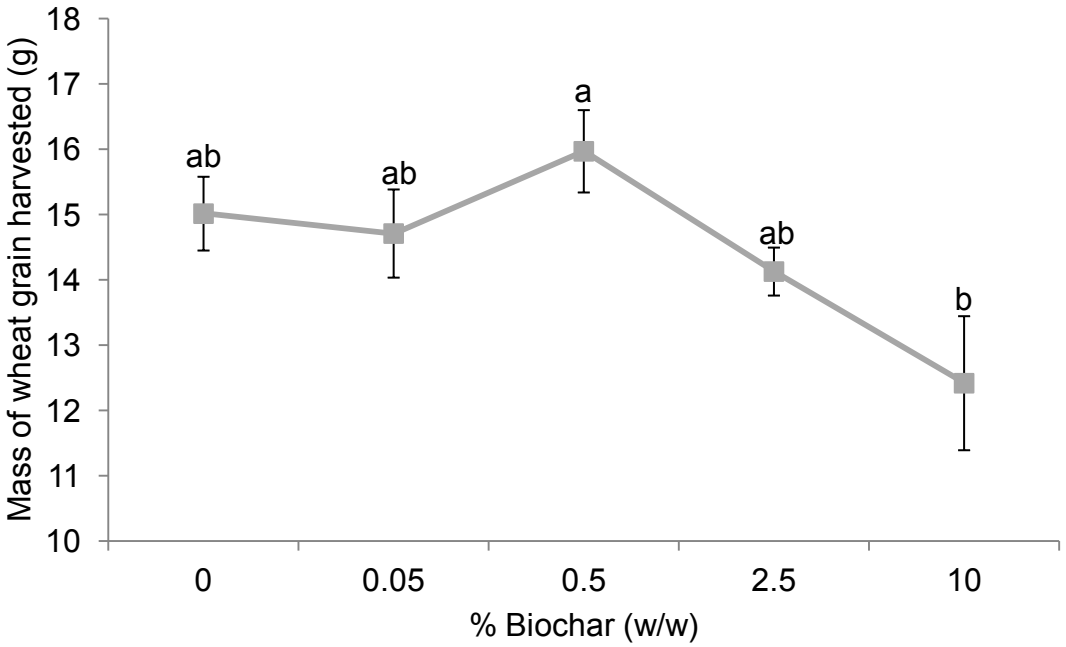


Figure 1.35 Average mass of wheat grain harvested per treatment at maturity.

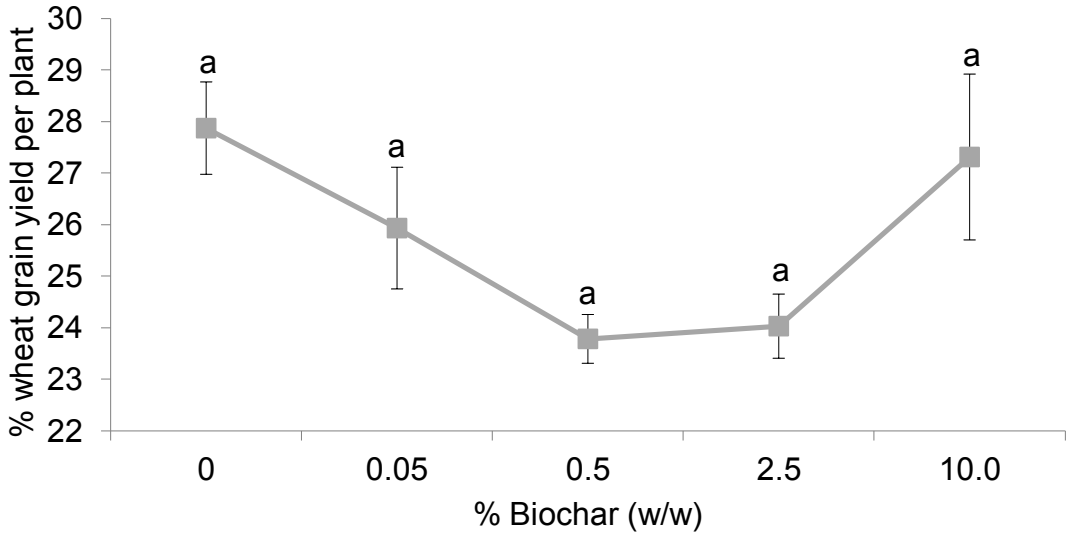


Figure 1.36 Average percentage wheat grain yield per plant per treatment at maturity.

A comparison of the 0.05 and 10.0 % treatments at maturity shows their shoot:root ratio was related (Fig. 1.37). According to Lehmann et al. (2011), an increase in the shoot:root ratio generally implies improved nutrient supply, which would translate into fewer roots being necessary to achieve similar above ground yields. This explanation supports the similarity of the percentage wheat grain per plant in both the 0.05 and 10.0 % fertilized mature wheat plants (Fig. 1.36). It is likely that at the 10.0 % biochar application level, the roots were stunted due to the waterlogged and anaerobic soil conditions. In contrast, as observed at the 0.5 and 2.5 % biochar application levels, the low shoot:root ratios may imply increased root development (Fig. 1.37).

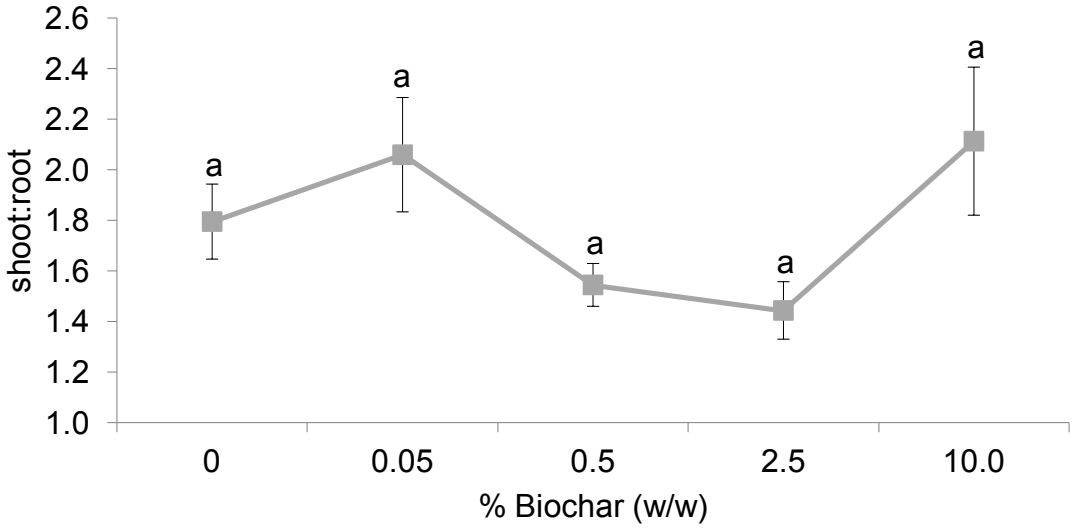
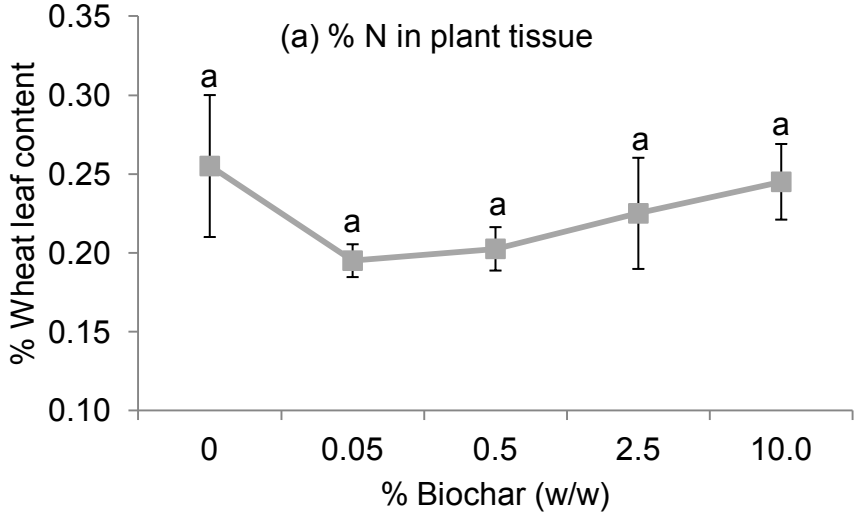


Figure 1.37 Comparison of the above and below ground biomass production of the mature fertilized treatments as the shoot:root ratio.

3.4.4.1 Effects of biochar on wheat nutrient uptake at maturity

Although N content slightly increased in the mature plant tissue (Fig. 1.38a), the results were similar to the 12 week wheat pot trial (Fig. 1.6b) in that N uptake decreased in the fertilized mature treatments when the biochar application level was above 0.5 % (Fig. 1.38b). As already established, this decrease may be attributed to a N deficiency. The P plant tissue content was similar to that of N. Phosphorus uptake in the fertilized mature treatments had a sharp decrease from the control to the 0.05% biochar application level (Fig. 1.39). The lowest P uptake occurred at the 0.5 % level, and thereafter, the P uptake marginally increased. As already mentioned, the pine biochar used in this study contains significant amounts of potassium (Table 1.5 and 1.6), this corresponds with the plant tissue and nutrient uptake of K as there was an increase with the biochar-amended treatments (Fig. 1.40).



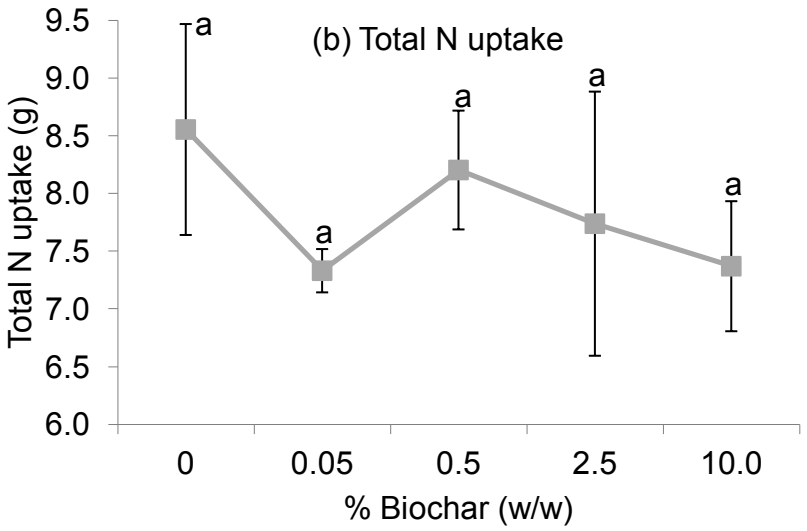
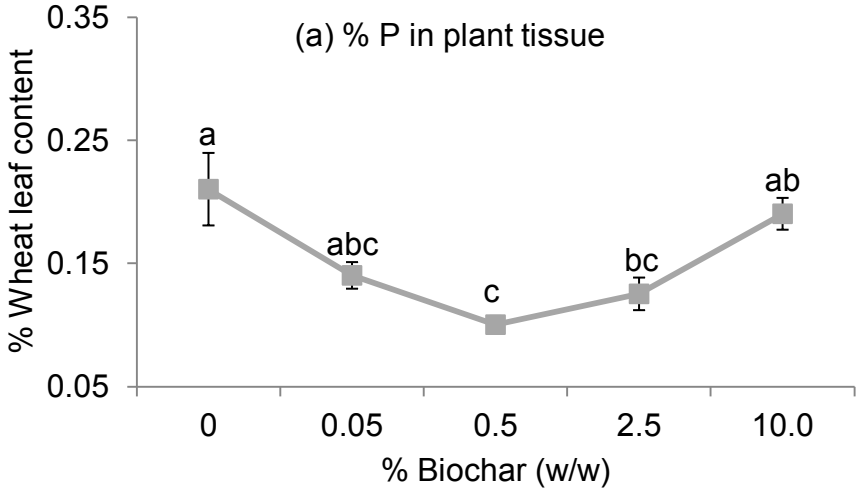


Figure 1.38 Nitrogen (a) wheat leaf content and (b) total uptake of the mature fertilized treatments.



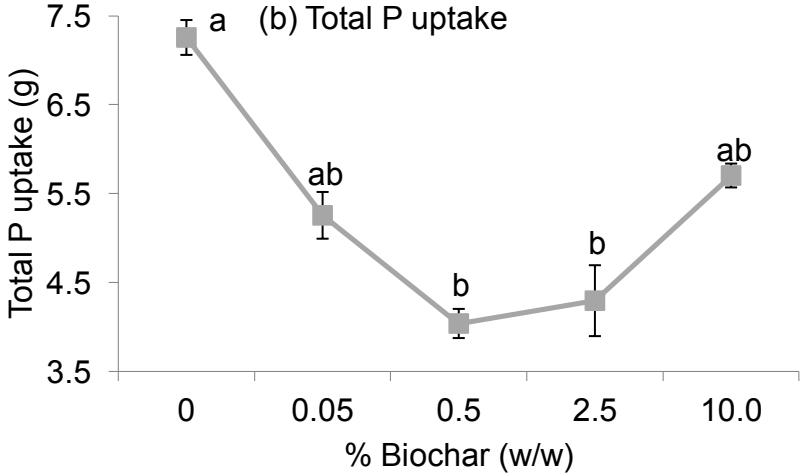


Figure 1.39 Phosphorus (a) wheat leaf content and (b) total uptake of the mature fertilized treatments.

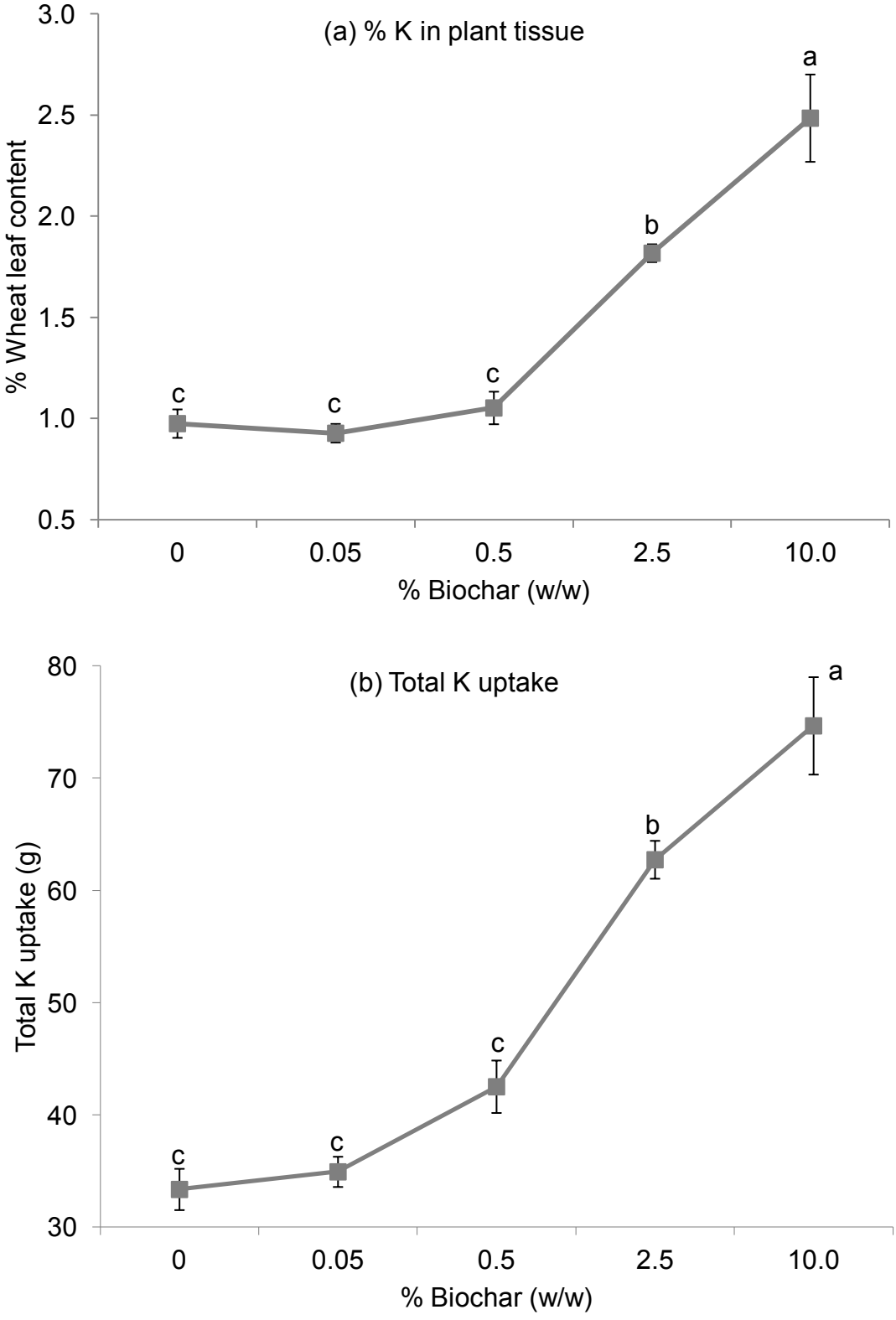


Figure 1.40 Potassium (a) wheat leaf content and (b) total uptake of the mature fertilized treatments.

Interestingly, although the control treatment, with its poor buffering capacity due to low clay activity, achieved the highest wheat grain yield per plant (Fig. 1.36), wheat grain did not translate into better quality grain in terms of grain protein content (Fig. 1.41). Another reason as to why the control treatment performed better than the biochar-amended soils, is likely that the control was not subject to the waterlogged and anaerobic soil conditions experienced at the higher biochar application levels.

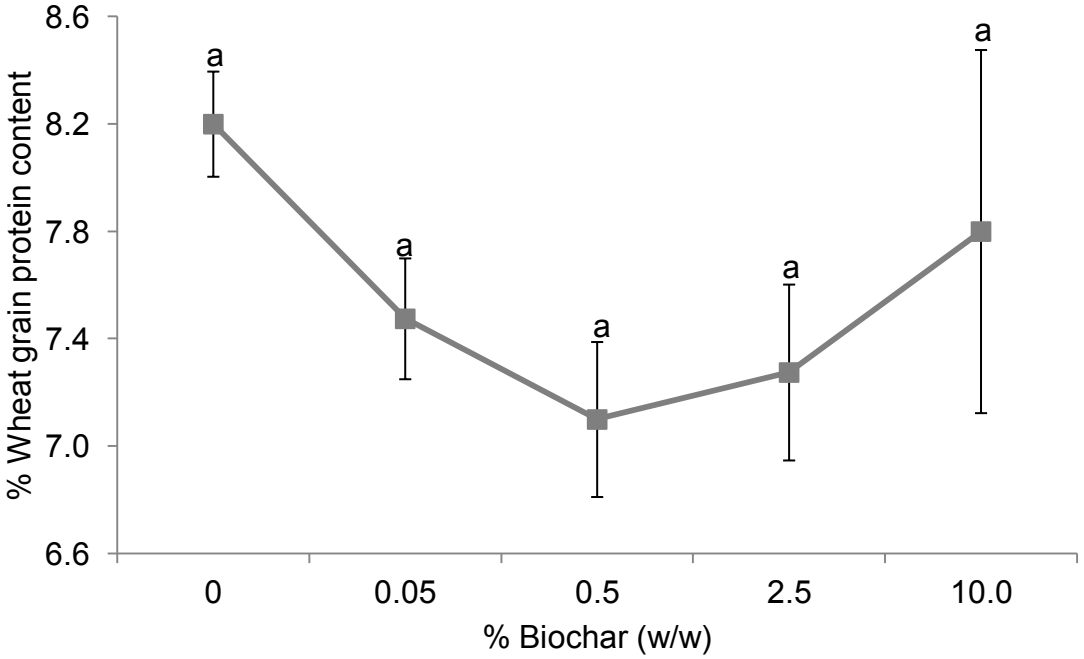


Figure 1.41 Percentage grain protein content of the fertilized wheat plants harvested at maturity.

Wheat grain harvested when the wheat plants reached maturity at 22 weeks was assessed by determining the grain protein content, K and P concentrations. Grain protein content is particularly important in defining wheat grain quality because a high protein content (>11 %) is a quality measure required by commercial bakeries to grade the bread produced to guarantee that it meets consumer standards (Killian and Burger 2008). The average grain protein content (Fig. 1.41) shows an inverse trend to the above ground biomass production (Fig. 1.34) possibly because the wheat plant initially invested more energy in vegetative (or above ground) growth. Subsequently, as the wheat plant was reaching maturity, the soil became depleted of nutrients, and therefore did not have sufficient N for grain production.

In addition, the total P and K determined from the wheat grain displayed a similar trend to grain yield. At the 10.0 % level, the percent protein, P and K levels all peaked with the highest overall concentrations in comparison to the other treatments

(Figs. 1.41, 1.42, and 1.43). It is suggested that the combination of biochar and a broad spectrum fertilizer were responsible for providing nutrients for wheat grain production. Also, since pine biochar inherently contains an abundance of K (Tables 1.7 and 1.9), it was expected that the 10.0 % biochar application level would have the highest K content.

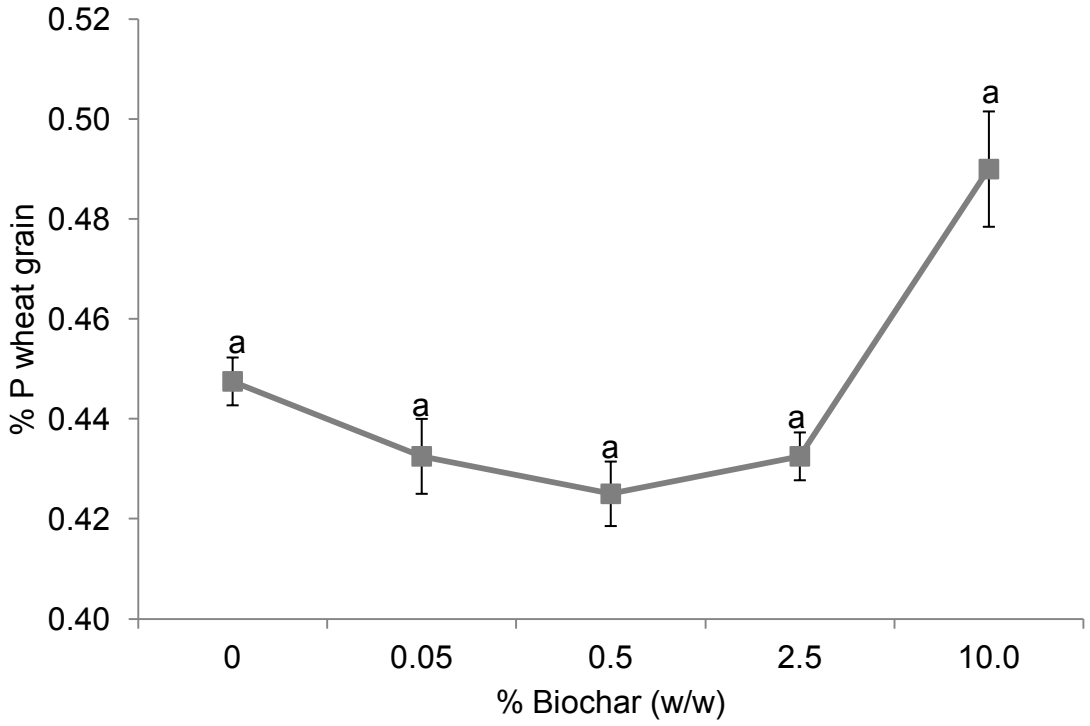


Figure 1.34 Percentage grain phosphorus content of the fertilized wheat plants harvested at maturity.

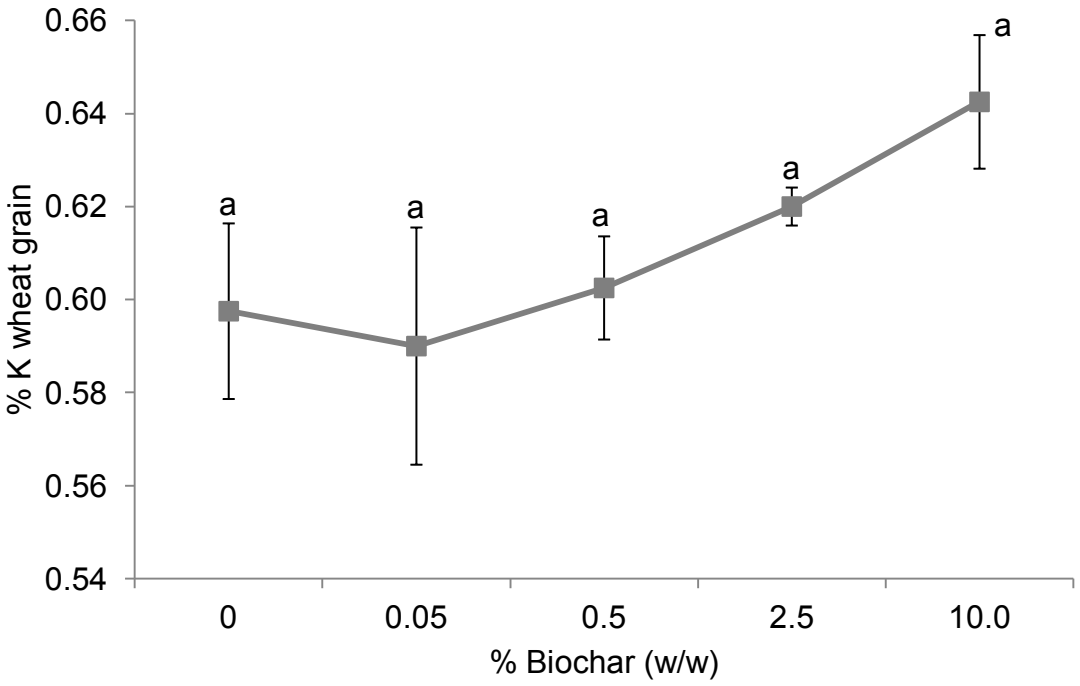


Figure 1.35 Percentage grain potassium content of the fertilized wheat plants harvested at maturity.

Vaccari et al. (2011) found that i) an increase in durum wheat grain yield ranged between 28 and 39 %, ii) the grain N content was not significantly affected by biochar amendment, and iii) a substantial increase in the grain protein content was observed. Given that grain protein content is an indicator defining wheat quality, it was further shown that N fertilizer uptake was higher in the biochar treated soils, than the control. Results from the current study did not indicate increases in grain yield due to the suggested N deficiency experienced. Therefore, these findings highlight the importance of N fertilizer use efficiency for wheat grain yield and quality.

3.5 Conclusions

Biochar immediately raises the soil pH when applied at increasing biochar application levels due to its alkalinity content. Therefore, caution should be taken when applying biochar to sandy soil as raising the pH over 6.50 (in water) results in over-liming and micronutrient deficiencies (Zn, Cu, and B). It also reduces the acid saturation percentage of the soil, which could contribute to greater above- and below ground biomass production. Biochar further keeps the soil wetter for longer due to its microporous nature, which would enhance nutrient uptake.

The current study showed that biochar-amended soils had improved biomass production in comparison to the control, no biochar added. Results showed that the unfertilized and fertilized treatments had the highest wheat above ground biomass production at the 2.5 and 0.5 % biochar (w/w) application levels, approximately 50 and 10 t ha^{-1} (15 cm depth), respectively. The unfertilized treatment showed a 29 % increase, whereas the fertilized treatment showed a 21 % increase. Since biochar reduced exchangeable acidity, increased soil pH of the acid soil, and inherently contains significant amounts of plant nutrients such as potassium, calcium and magnesium, it is suggested that these are the main reasons for enhanced plant growth. In particular, the high manganese uptake efficiency at the 2.5 % level may have contributed to the optimum biomass production in the absence of fertilizer. Whereas, the 0.5 % level most likely experienced optimum growth due to increased K uptake, and the relatively neutral soil pH of 6.80 (in water) before planting, which did not cause micronutrient deficiencies incited by high soil pH. In contrast, the inhibited plant growth at the 10.0 % biochar (w/w) level was probably due to the over-limed and wetter soil conditions, together with nutrient deficiencies of nitrogen, phosphorus, zinc, boron, manganese and copper.

Increasing the biochar application levels increased the C:N ratio of the soil and appeared to reduce N uptake probably because of nitrogen immobilization. This might only be a short-term effect; once the more labile (volatile carbon component) of the biochar is degraded, then this should reduce immobilization. Therefore, the exclusive use of biochar in the absence of N fertilizer is not encouraged. In addition, because our results provided evidence of micronutrient deficiencies due to over-liming, it is recommended that biochar not be applied on acidic, sandy soils at levels greater than 0.5 % biochar (w/w), approximately 10 t ha^{-1} at 15 cm depth.

Considering the positive and negative plant responses obtained in this study, a long-term field trial of biochar is strongly suggested. This would facilitate a clearer understanding of the changes in nutrient availability and alkalinity in soil over time due to the addition of biochar.

Research on the application of biochar as a soil amendment has to date not been conducted in South Africa, thus highlighting the importance of this study. The use of slow release fertilizers in biochar-amended soils has also not been investigated. Furthermore, the effect of biochar on the efficiency of organic N fertilizers is an unexplored area of study.

CHAPTER 4

4 An Investigation on the Effect of Biochar on Nutrient Mobility

4.1 Introduction

A major problem related to sandy soils in the Western Cape Province is a high rate of nitrogen leaching to shallow groundwaters causing contamination hazard and potentially restricting groundwater use (Jovanovich et al. 2008). Several options have been proposed for reducing nutrient leaching in agriculture. Lehmann et al. (2003) proposed that nutrient leaching reductions are possible through either the application of slow-release forms of fertilizers, or increasing adsorption sites for longer retention of applied fertilizers. The continuous application of fertilizer during the growing season, specifically timed to supply nutrients during crop growth stages of maximum water and nutrient uptake, has also been suggested as a means to combat increased nutrient leaching (Laird et al. 2010). However, these options are all costly short-term solutions to the problem of mineral fertilizer leaching (Laird et al. 2010).

Biochar has been suggested as an effective, long-term tool for reducing the adverse impacts of mineral fertilizer leaching on surface and groundwater quality (Lehmann et al. 2003; Steiner et al. 2008). The amendment of sandy soils with biochar is especially beneficial as research has shown it to provide greater water holding capacity (Tryon 1948). Empirical evidence suggests that the retention of soil water, and certainly nutrients, together with the increase in electrostatic adsorption sites is possible through biochar additions (Lehmann et al. 2003).

In recent years, most of the biochar research on nutrient leaching has been studied parallel with the application of either inorganic or organic N fertilizer sources. In a 70 day laboratory study investigating the influence of bamboo charcoal (biochar) applied at 0.5 % (w/w) on N retention at different soil depths using multi-layered soil columns, the application of an inorganic N source, ammonium chloride (NH_4Cl) applied at 400 kg N ha^{-1} was explored (Ding et al. 2010). At the 10 cm depth, the bamboo charcoal treated sandy-silt soil showed a delay in the ammonium nitrogen (NH_4-N) concentration in the leachate. It was reasoned that because charcoal has a

highly porous structure, leaching of NH_4-N was reduced because of the ability of charcoal's adsorptive properties. Furthermore, between the 0 and 20 cm column depth, it was found that biochar retained NH_4-N for a longer time period. This provided evidence that biochar addition to soils may delay inorganic NH_4-N leaching, and thus benefit crops for optimal N utilization.

Recent studies have also been conducted on the effect of N leaching on organic N sources. Laird et al. (2010) investigated the application of 5 g kg^{-1} swine manure on a fine-loamy agricultural soil with mixed hardwood derived biochar applied at 0, 5, 10 and 20 g kg^{-1}. The impact of the biochar was investigated on nutrient leaching over a long-term, 45 week laboratory study. It was found that biochar effectively reduced nitrate (NO_3) leaching losses within two weeks for the control 0, 5 and 10 g kg^{-1} biochar treated soil columns receiving no manure. These soils measured about 1 mg of NO_3-N per column per week and remained relatively unchanged until the termination of the experiment at 45 weeks. On the contrary, the control soils receiving 20 g kg^{-1} biochar and no manure lost 2 mg NO_3-N per column per week. By the end of week 45, mineralization of organic N induced by the high biochar application level of 20 g kg^{-1} biochar instigated a total of 26 % more NO_3-N loss in the 20 g kg^{-1} biochar treated soils relative to the 0, 5 and 10.0 g kg^{-1} treatments. In summary, the results from the study highlighted that the manure treated soils receiving biochar reduced total inorganic N (NO_3 and NH_4) by 11 % in comparison to the manure treated soils receiving no biochar.

Biochar has been shown to possess great potential in reducing N losses by means of nutrient leaching experiments. In view of the research that has been published concerning N leaching, we have identified some gaps in knowledge. Little information is available on the effect of biochar on leaching of NO_3 and basic cations from inorganic fertilizers in sandy soils. Furthermore, the availability of nutrients remaining in the biochar-amended soil after leaching remains to be investigated.

4.2 Objectives

The main aim of this study was to examine the effect of locally produced biochar on potentially reducing or preventing leaching of inorganic fertilizer in a typical Western Cape acidic, sandy soil. In addition, the study looked at the leaching of nutrients

contained in biochar after application to the soil. We also investigated the amounts of plant available inorganic N remaining in the soil and biochar-amended soil after the leaching period.

4.3 Materials and methods

4.3.1 Soil and biochar

The two fertilizer leaching experiments were conducted using the soil and biochar described in Chapter 3 (Section 3.3.1). In the first experiment, the effect of biochar on the leaching of ammonium nitrate (NH_4-NO_3) was studied, while in the second experiment, the effect of biochar on the leaching of a multi-element fertilizer was studied.

4.3.2 Preparation of soil columns

Soil columns with dimensions of 10.5 cm inner diameter and 25 cm lengths were constructed using PVC pipes and fitted with PVC end caps. The column tops were kept open to prevent anaerobic conditions from building up. Prior to packing the columns, a coat of PVC paint was applied on the inner column wall and coated with coarse sand to help minimize preferential flow paths. A small amount of glass wool was placed in the drain pipe opening at the base of the column to prevent soil-biochar from leaching out. In addition, a 2 cm thick layer of coarse sand was placed in the bottom of each column to further prevent soil loss through the large opening. Sieved (<2 mm) air dried soil, and biochar (oven dry weight equivalent) were mixed and thoroughly homogenized. The soil columns were packed with 2.0 kg of (biochar treated or untreated) soil by tamping the columns as the soil was added. All columns were carefully packed to achieve an initial bulk density of about 1.5 g cm^{-3}. All treatments were replicated three times.

In the N leaching experiment, there were three biochar treatments (0.5, 2.5, and 10.0 % biochar w/w) and a control (no biochar added).

In the multi-element leaching experiment, the treatments were as follows: two control (sand only) treatments, one with fertilizer added and one with no fertilizer added; and two biochar-treated soil treatments (0.5 % biochar w/w), one with

fertilizer added and one with no fertilizer added. The purpose of having two control treatments was to determine, by subtraction, the amount of nutrients leaching inherently from the biochar and the added fertilizer in comparison to the fertilized and unfertilized sand only columns.

4.3.3 Soil column incubation and leaching experiment

The columns were incubated under laboratory temperature and relative humidity conditions. The weekly leaching events were designed to simulate winter rainfall patterns of heavy rainfalls of 60 mm (Agricultural Research Council, Agromet – ISCW), which is equivalent to 520 mL of water based on the leaching columns surface area. The water was added from the top of the column through burettes mounted above the middle of each column. Filter paper was placed on the soil surface to help dissipate the water drops as they impacted on the upper surface of the columns. The columns were freely draining during the duration of the leaching study, and all leachate samples were collected in Erlenmeyer flasks covered with laboratory film in order to minimize evaporative water loss.

4.3.3.1 Experiment 1: Inorganic nitrogen leaching study

A single fertilizer application of 100 mg NH_4-NO_3 was applied in each column as a solution. This is approximately equal to the typical N fertilizer recommendation of 100 kg N ha^{-1} for winter wheat in the Western Cape. The fertilizer was dissolved in 5 mL distilled water, and applied evenly in drop form to the surface area of each column.

Leachates were collected, weighed and analyzed once weekly for 6 weeks to determine the release rates of the N fertilizer. The leachate pH and electrical conductivity (EC) were subsequently measured. Leachate samples were filtered through Whatman 42 filter paper and analyzed for ammonium (NH_4^+) using a colorimetric method (Mulvaney 1996), and for NO_3^- by ion chromatography (IC). Cumulative leaching for the 6 week study was calculated from the measured leachates, and the NH_4-N and NO_3-N amounts were collectively added.

At the end of the 6 week N leaching study, further analyses were performed on the leached soil and soil-biochar treatments. The soil in each column was thoroughly mixed and sampled in duplicate. The plant available inorganic N (NH_4 and NO_3)

remaining in the soil was determined by a 2 M KCl extraction. The NH_4-N was determined colorimetrically, and the NO_3-N was also determined colorimetrically (cadmium-reduction method) (Mulvaney 1996).

4.3.3.2 Experiment 2: Multi-element leaching study

A single fertilizer application of 75 mg of the multi-element fertilizer Chemicult Hydroponic Nutrient Powder (Starke Ayers, South Africa) was applied in each column as a solution (Table 2.1). This quantity is approximately equal to the macronutrient (K, P, Ca, Mg and S) fertilizer recommendation for winter wheat in the Western Cape region. The fertilizer was dissolved in 5 mL distilled water, and applied evenly in drop form to the surface area of each column. For the purpose of this study, only a selected few elements were investigated, namely the macro-elements K, P, Ca and Mg, the non-essential element Na, and the micro-elements Fe, Mn and Zn.

Table 2.1 Elemental composition of the multi-element fertilizer (Chemicult) used in the multi-element leaching study.

Macro-elements	%	Micro-elements	%
N	6.50	Fe	0.150
K	13.0	Mn	0.024
P	2.70	B	0.024
Ca	7.00	Zn	0.005
Mg	2.20	Cu	0.002
S	7.50	Mo	0.001

Including 0.077 % of the non-essential element Na.

Leachates were collected, weighed and analyzed once weekly for 6 weeks to determine the release rates of the K, P, Ca, Mg, Na, Fe, Mn and Zn from the fertilizer. The leachate pH and EC were subsequently measured. Leachate samples were filtered through Whatman 42 filter paper and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using the Thermo ICap 6300 radial instrument. Cumulative leaching for the 6 week study was calculated from the measured leachates.

4.4 Results and discussion

4.4.1 Inorganic nitrogen leaching study

4.4.1.1 Average leaching volume

The biochar (BC) used in the current study has already been shown to have a high water holding capacity (Chapter 3, Section 3.3.4). This property of biochar again became apparent when during week 1 of leaching; decreasing volumes of water were collected with increasing biochar application levels (Table 2.2). At the 10.0 % biochar (w/w) treatment, no leachates were collected during the first week (Fig. 2.1). The average weekly leachate volume collected for each treatment marginally increased from week 1 to week 5, and during week 6, approximately 90 % of the water applied was leached across all the treatments (Table 2.2).

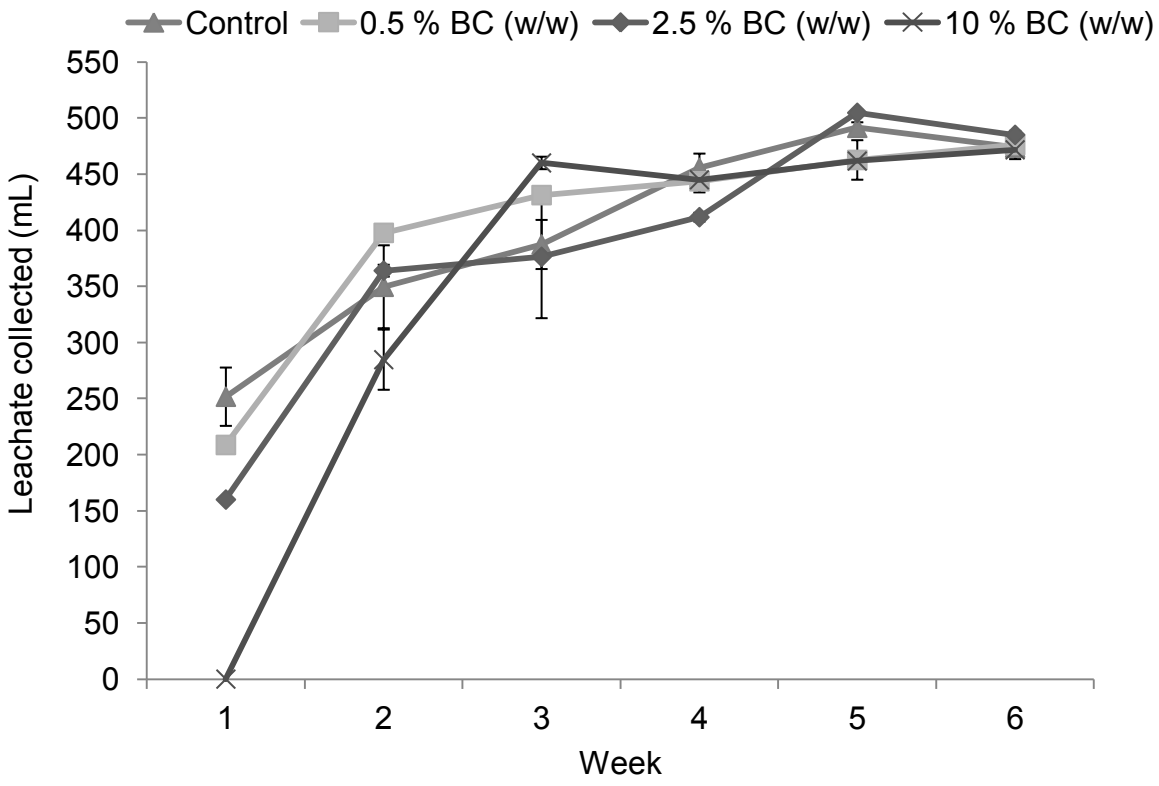


Figure 2.1 Average weekly volumes (mL) of leachates collected from the N leaching study experimental columns with control, no biochar added, and biochar-amended soils. All columns were fertilized with 100 mg ammonium nitrate. The weekly volume of water leached for each treatment was significant at the $P < 0.05$ level based on the two factorial analysis of variance (ANOVA) with replication.

Table 2.2 Average percent of inorganic nitrogen fertilizer leachates collected of the total amount of water applied per treatment over six weeks.

% Biochar (w/w)	% Water leached of total water applied per week					
	1	2	3	4	5	6
0	48	67	74	88	94	91
0.5	40	76	83	85	89	92
2.5	31	70	72	79	97	93
10.0	0	55	88	86	89	91

The 10.0 % treatment showed an 11.9 % difference in the final volume of water collected (Fig. 2.2). This means that less water came out of the 10.0 % treatment. This was attributed to the high field capacity (Chapter 3, Section 3.3.4) and increased micro-porosity offered by the biochar. The amount of cumulative water leached from the 0.5 % biochar (w/w) columns was not significantly different relative to the control (Fig. 2.2). In summary, the volume of water collected by the end of week 6 was comparatively similar between treatments (Figs. 2.1 and 2.2). This implies that the amount of leaching was uniform and consistent without the interference of preferential pathways.

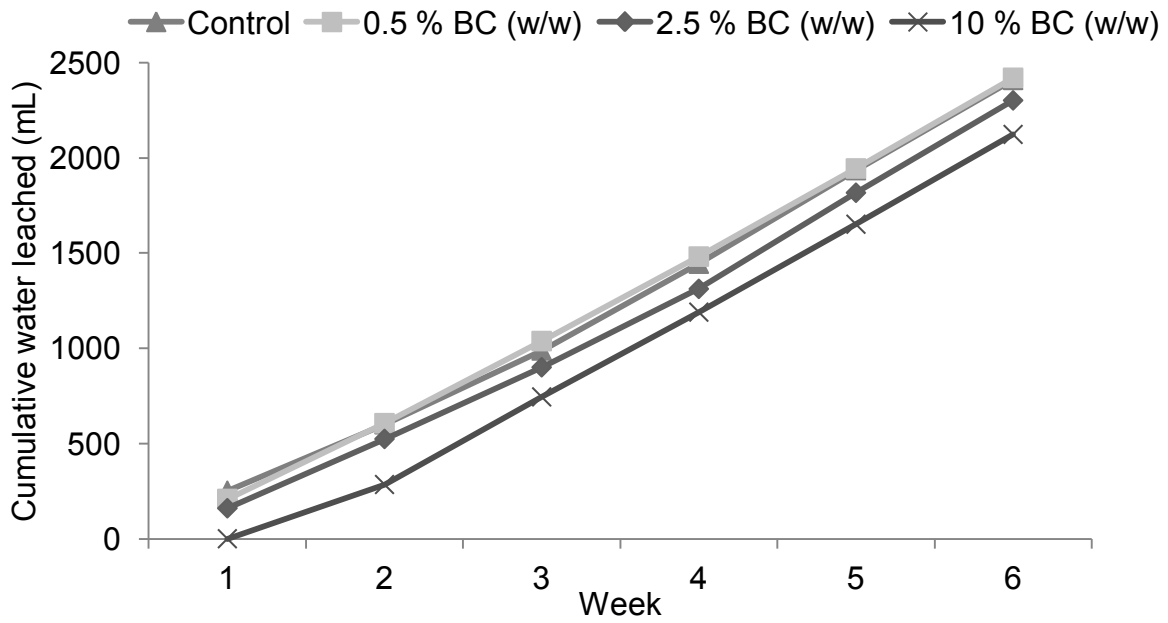


Figure 2.2 Cumulative water leached over the six week duration of the N leaching study. The cumulative volume of water leached for each treatment was significant at the P <0.05 level based on the two factorial analysis of variance (ANOVA) without replication.

4.4.1.2 The leachate pH and EC measurements

Weekly pH measurements of the N leaching study leachates behaved differently at the various treatments (Fig. 2.3). The control and 0.5 % treatments initially had pH values of 5.74 and 6.29 respectively. During week 2, these pH values dropped to 5.21 and 5.96 respectively. This decrease is likely as a result of the acid forming nature of ammonium since nitrification generates acidity (McBride 1994) from the NH_4-NO_3 fertilizer. It is suggested that the NH_4 salts only caused the initial decrease in pH at the 0 and 0.5 % treatments because of their poor buffering capacities. From week 3, the increase in pH at the control and 0.5 % treatments is attributed to reduction reactions occurring over time. Thereafter, the pH remained relatively constant between weeks 5 and 6.

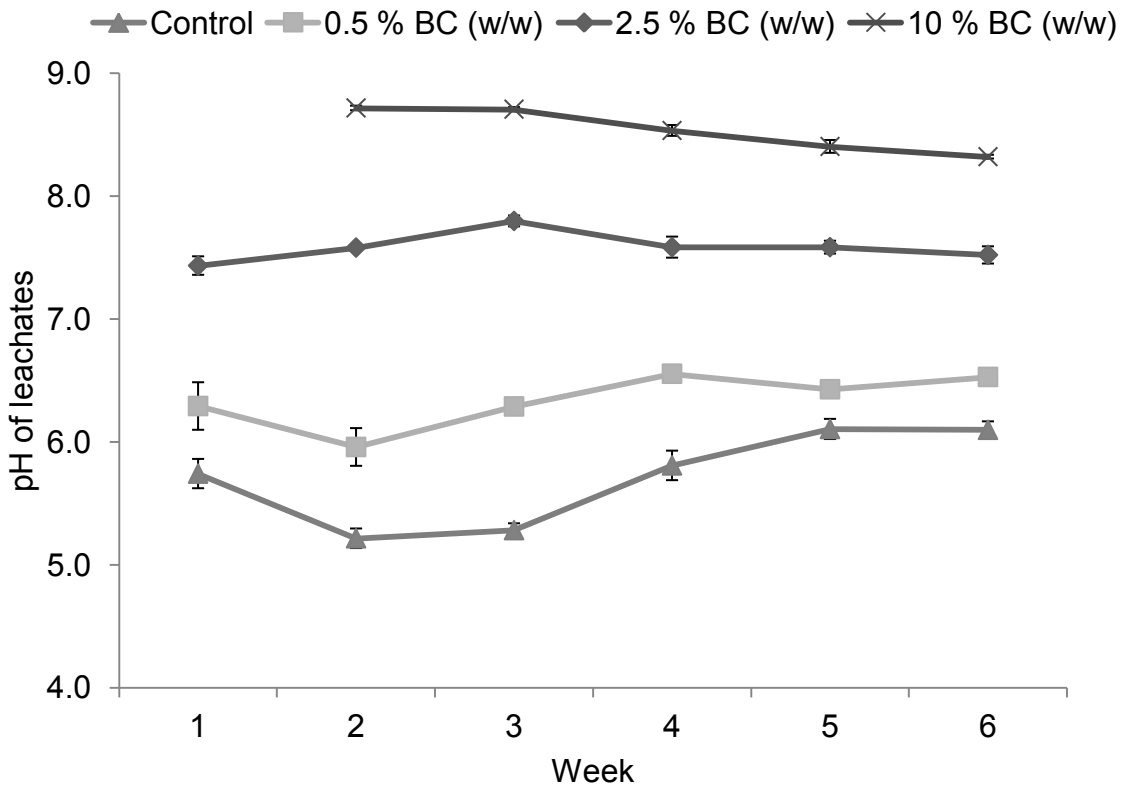


Figure 2.3 Weekly pH measurements of the N leaching study. The individual pH values for each replicate treatment were significant at the P <0.05 level based on the two factorial analysis of variance (ANOVA) with replication.

The results from the current study showed a gradual decline of EC from week 3 of the leaching study, with an average EC value of 0.464 dS m^{-1} across all biochar treatments except the 10.0 % treatment (Fig. 2.4). This observation correlates with N fertilizer breakthrough curves. The control and lowest biochar application treatment

of 0.5 % (w/w) showed similar tendencies throughout the six week study. The initial sharp EC value at the 2.5 % (w/w) treatment did not differ significantly from other values. It was attributed to either the high concentration of dissolved salts at the 2.5 % level, or due to column-to-column variability. No leachates percolated during week 1 of leachate collection at the 10.0 % level. From the second to the fourth week, the EC values steadily increased from 0.243 to 0.593 dS m^{-1}, and thereafter slowly decreased. This pattern is possibly due to the initial increase, followed by a decline over time of the total soluble salts.

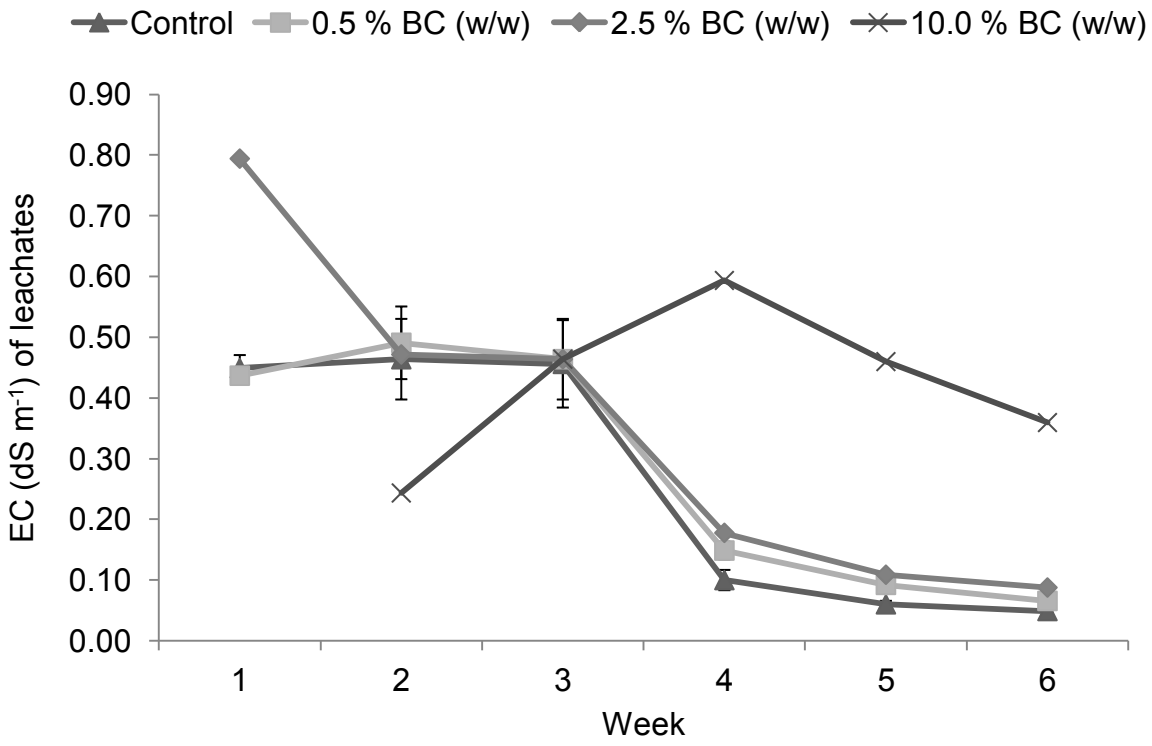


Figure 2.4 Electrical conductivity in the leachate of the inorganic N fertilizer leaching study carried out over six weeks.

Ding et al. (2010) described the EC in leachates as a measure of the risk of groundwater pollution by dissolved ions. Their results confirmed that bamboo charcoal evidently reduced leaching due to the ability of biochar to adsorb different ions by exchange mechanisms and physical adsorption. Furthermore, their results showed that the vertical movement of dissolved ions was significant, and was caused by the adsorption effect of biochar.

4.4.1.3 Cumulative ammonium leaching

Biochar significantly reduced the leaching of ammonium by 12, 50, and 86 % in the 0.5, 2.5, and 10.0 % treatments, respectively, compared to the control treatment (Fig 2.5a). From the 100 mg of NH_4-NO_3 fertilizer applied in each column, 22.5 mg was NH_4-N (atomic mass equivalent). The control and 0.5 % biochar (w/w) application treatments behaved similarly concerning the weekly cumulative leaching of NH_4-N (Fig. 2.5a). During the first two weeks of leaching, the average amount of NH_4-N leachate was approximately 5 and 15 mg. Thereafter, there was a steady increase in cumulative NH_4-N until the amount became relatively constant from week 4. The 2.5 % biochar (w/w) treatments showed that about half of the NH_4-N was leached in comparison to the 0.5 and 10.0 % treatments. At the 10.0 % biochar (w/w) treatment, approximately 5 mg NH_4-N was cumulatively leached (Fig. 2.5a).

4.4.1.4 Cumulative nitrate leaching

Biochar reduced the leaching of nitrate by 26, 42, and 95 % in the 0.5, 2.5 and 10.0 % treatments, respectively, compared to the control treatment (Fig 2.5b). The 100 mg of NH_4-NO_3 fertilizer added in each column was in effect 77.5 mg NO_3-N (atomic mass equivalent). Between weeks 1 and 3, there was a sharp increase in the amount of nitrates leached in the control columns (Fig. 2.5b). Thereafter, no further significant weekly NO_3 losses were observed. Instead, all of the treatments reached relatively constant amounts of NO_3-N leached for the remainder of the study.

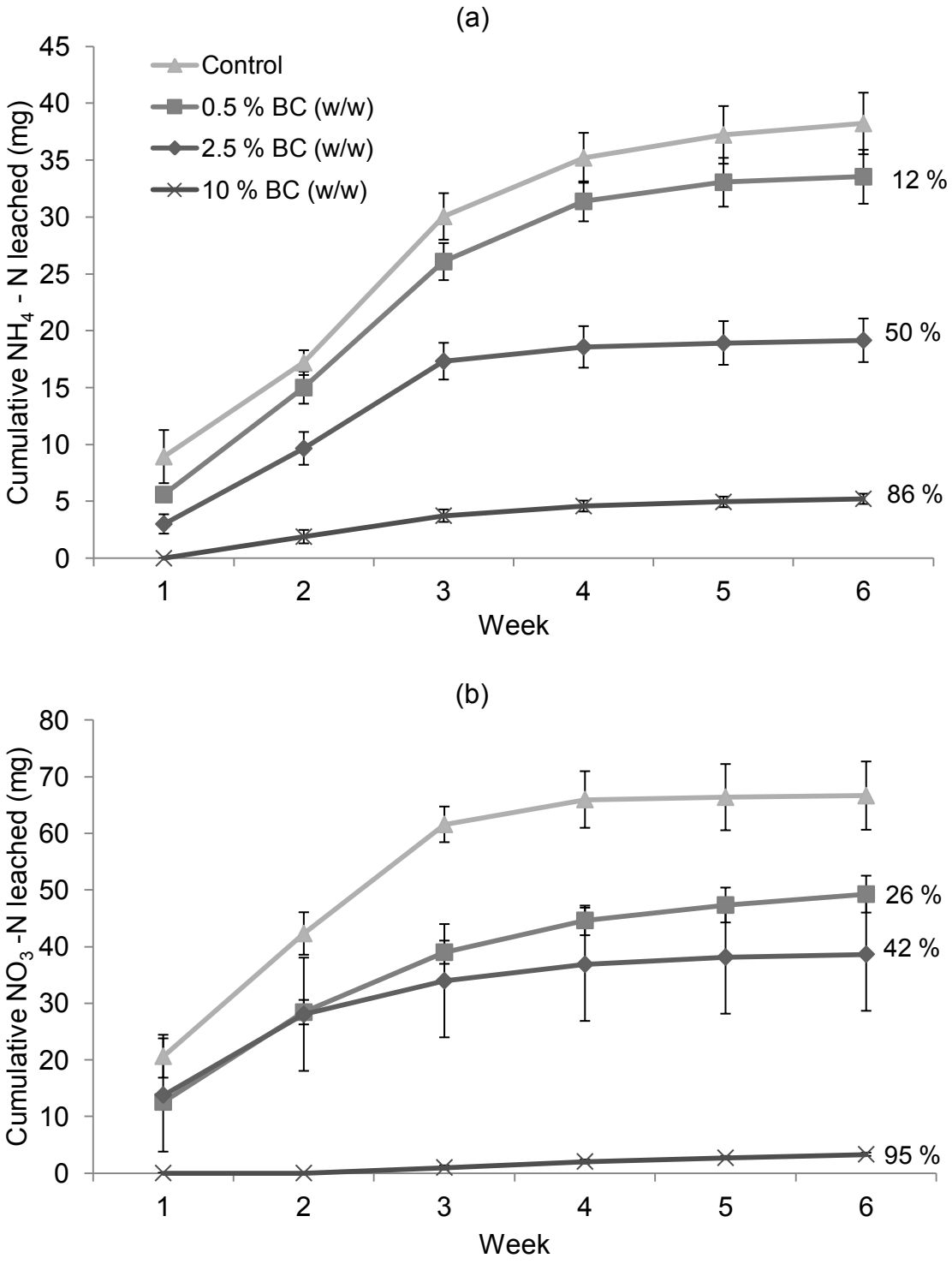


Figure 2.5 Cumulative N leaching losses of (a) ammonium-nitrogen and (b) nitrate-nitrogen from columns without biochar (control) and treated with biochar at 0.5, 2.5, and 10 % (w/w) application treatments over six weeks. The percentages indicate the relative % difference of N leaching from the control. The individual N values for each replicate treatment were significant at the $P < 0.05$ level based on the two factorial analysis of variance (ANOVA) with replication.

Since the ammonium- and nitrate nitrogen cumulative leachates followed a relatively constant pattern between weeks 4 and 6 of the study, it is suggested that most of the fertilizer had already come out. This implies that further than the end of week 6, there would have been no additional increases in N leaching because most of it had already leached out. Therefore, it is suggested that a time period of 6 weeks was potentially sufficient for biochar to reduce N leaching.

4.4.2 Plant available (2 M KCl) extraction

The 2 M KCl extraction performed at the end of the leaching period was aimed at determining the potentially plant available N (NH_4 and NO_3). The results show that it is likely that a fraction of the applied NH_4-NO_3 may be trapped, and thus plant available (exchangeable) (Table 2.3). Although soils may appear typically high in total N as indicated by the 2 M KCl extraction, many soils are in effect characteristically low in plant available N. In addition, although the 2 M KCl extraction gives an indication of the potentially plant available N, the remaining inorganic N which was neither potentially plant available nor leached, may be denitrified, temporarily immobilized, fixed or volatilized.

Figure 2.6 illustrates the possible fates of the inorganic N forms (NH_4-N and NO_3-N) as i) potentially plant available as determined by the 2 M KCl extraction at the end of the 6 week study, ii) leached N and iii) fixed or volatilized N. The sandy soil used in this study contained 0.16 % C and 0.03 % N. Thus, it is likely that mineralization of some of the inherent soil organic matter (OM) contributed to the additional ammonium leached out of the control and 0.5 % treatments (Fig. 2.6a). A further possible source of the extra ammonium may be due to denitrification of the nitrate fertilizer added.

The control soil, no biochar added, showed that the contributions of the inherent soil N, in combination with fertilizer, were sufficient to potentially provide approximately 0.3 and 10.7 mg of the originally added NH_4-N and NO_3-N, respectively, for plant uptake (Table 2.3). This means that the sandy soil contributed approximately 1.3 % of the potentially plant available N in the form of NH_4-N, whereas, the remaining 13.8 % is from NO_3-N (Fig 2.6). All of the NH_4-N applied as inorganic N fertilizer was

leached (Table 2.3) and over 70 % NH_4-N was possibly leached from soil OM. Neither NH_4-N nor NO_3-N was fixed or volatilized at the control treatments (Fig. 2.6).

The lowest level of biochar-amended soil, 0.5 %, showed that all of the possibly exchangeable remaining N was from NO_3-N (Fig. 2.6). The reason as to why no NH_4-N was detected from the 2 M KCl extraction is because it may have all converted to NO_3-N due to nitrification (Havlin et al. 2005). The NO_3-N contents at this level suggested that 14.9 % was plant available, 63.4 % was leached, and 21.7 % may have either been fixed or volatilized. Similar to the control treatment, no NH_4-N was found to be fixed or volatized, instead, an additional 49.2 % was leached, possibly from soil OM.

The largest contribution of the fate of NH_4-N at the 2.5 % treatment was attributed to 86 % leaching loss. Similar to the 0.5 % treatment, an application of 2.5 % biochar (w/w) prompted less NH_4-N relative to NO_3-N to be potentially plant available. Again, nitrification is suggested as to why there was more NO_3-N than NH_4-N. Nitrate nitrogen showed that one fifth of the 2.5 % biochar treated soil could possibly contribute to plant available nitrates. Fifty percent NO_3-N was leached at this level, and the remaining 30 % may have been fixed or volatilized. The remainder of the NH_4-N was suggested to be plant available and only 2.4 % NH_4-N was found to be fixed or volatilized (Fig. 2.6).

At the highest level of biochar application, NH_4-N contributed the greatest fraction of 64.6 % as plant available, while for NO_3-N, 79.4 % was calculated as being fixed or volatilized (Fig. 2.6). The inorganic N forms totalled NH_4-N leaching losses of 23.1 % and NO_3-N losses of 3.7 %. Furthermore, at the 10.0 % level, it is possible that the inorganic N may have followed one of two fates. Firstly, since less NO_3-N was extracted as potentially plant available relative to NH_4-N, it is likely that denitrification took place. This is suggested as the plant available N may have been reduced to NH_4^+ by denitrifying bacteria as a result of the wetness of the leaching columns. Secondly, it is suggested that temporary N immobilization may have occurred due to stimulated microbial activity (Laird et al. 2010; Lehmann et al. 2003) caused by the high C:N ratio (Chapter 3, Table 1.3).

Ding et al. (2010) found that the addition of NH_4-N was advantageous in that it was retained in the upper 0 - 20 cm for a long time, thereby contributing to more effective N utilization by crops. Similarly, the results from the current study show that the highest biochar application treatment recovered about 152 % more plant available N than the control soil, with no biochar added. These findings provide evidence that reduced N leaching due to the effects of applied NH_4^+ result in electrostatic adsorption on the exchange sites (Steiner et al. 2008). Additionally, because the pine wood sawmill waste biochar used in this study had a high surface area of 346.42 m^2 g^{-1}, it has been shown that a high biochar surface area is a beneficial ion adsorbent of organic molecules and associated nutrients (Steiner et al. 2008). Therefore, biochar has prospective as a soil amendment that retains nutrients as a result of its adsorption properties and ability of reducing N leaching losses over time.

Furthermore, because not all of the nitrates were leached by the end of the 6 week study, it is suggested that although biochar can reduce inorganic N leaching from soils, it cannot effectively reduce leaching within the short term. This reasoning is supported by research conducted by Singh et al. (2010) where it was found that NH_4 and NO_3 (applied at 90 kg N ha^{-1}) leaching from two contrasting soils (an Alfisol, and a Vertisol) was not complete within 8 weeks. Therefore, a longer leaching period and a more detailed study measuring gaseous losses is suggested to fully understand the consequence of leaching on soils. As a result, it is maintained that the fate of the remaining inorganic N fertilizer may have either been i) trapped in the biochar, ii) temporarily immobilized by microbes (iii) denitrified to other forms of nitrogen or iv) volatilized.

An attempt was made to quantify the total inorganic N contents still remaining in the soil at the termination of the leaching events. However, neither the dry combustion using the EuroVector Elemental Analyzer 3000 series, nor the Kjeldahl methods were sensitive enough to detect any significant differences between treatments. Thus, this highlights an issue that needs to be overcome in future studies.

Table 2.3 Nitrogen balance analysis for both NH_4-N and NO_3-N) recovered from column leachates.

% Biochar (w/w)	NH_4-N (mg)				NO_3-N (mg)			
	Applied	Leached	2 M KCl	Fixed or volatilized	Applied	Leached	2 M KCl	Fixed or volatilized
0	22.5	38.3 a	0.3 a	-16.1 a	77.5	66.2 a	10.7 a	0.59 c
0.5	22.5	33.6 a	0.0 a	-11.1 a	77.5	49.1 b	11.6 a	17 b
2.5	22.5	19.3 b	2.7 a	0.5 a	77.5	38.7 b	15.9 a	23 b
10.0	22.5	5.2 c	14.5 a	2.8 a	77.5	2.9 c	13.1 a	62 a

Means in the same column followed by the same symbol are not significantly different at $P < 0.05$ level based on Tukey's Studentized Range test.

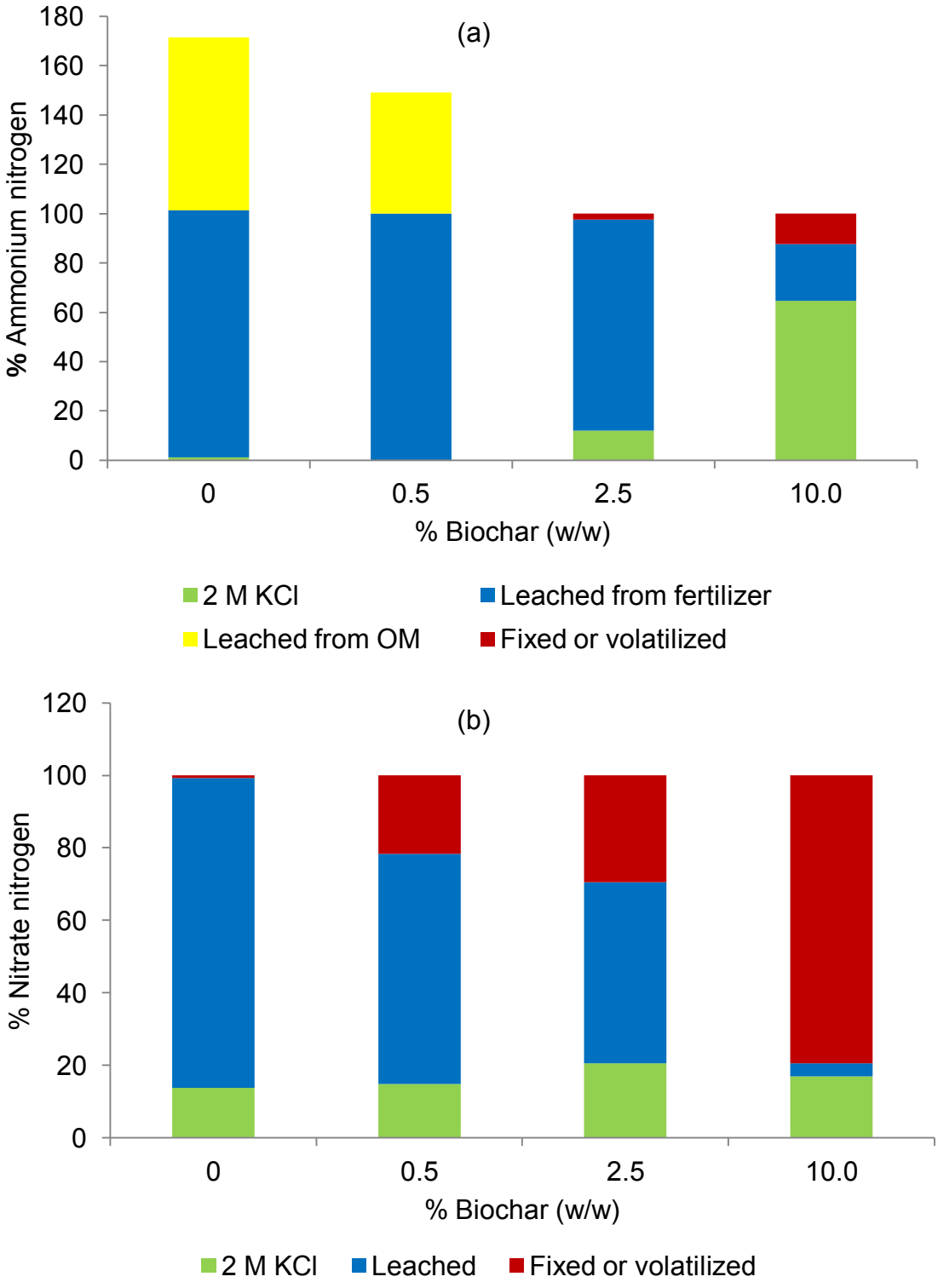


Figure 2.6 Soil leaching columns illustrating the possible fate of the inorganic N forms as a) ammonium nitrogen and b) nitrate nitrogen. The additional ammonium nitrogen leached (a) is potentially from organic matter (OM). The fate of the NH_4-NO_3 fertilizer applied was quantified relative to the total amount applied as either being i) potentially plant available N, as determined by the 2 M KCl extraction, ii) leached throughout the six week leaching study, and iii) fixed or volatilized.

4.4.3 Multi-element leaching study

4.4.3.1 Average leaching volume

The volume of leachates collected during week 1 of the study was much more for the soil columns without fertilizer relative to the soil columns with fertilizer (Fig. 2.7 and Table 2.4). The leachates collected from soil columns without fertilizer application showed no significant differences throughout the 6 week study (Fig. 2.7). During week 2, the volume of leachates collected for all treatments was similar with an average volume of 475 mL (Fig. 2.7) and also similar with mostly 91 % water leached of the total volume of water applied (Table 2.4). By week 6, similarly to the results observed in the current study (Section 4.4.1.1), the volume of leachates collected was relatively similar across all treatments (Figs 2.7 and 2.8).

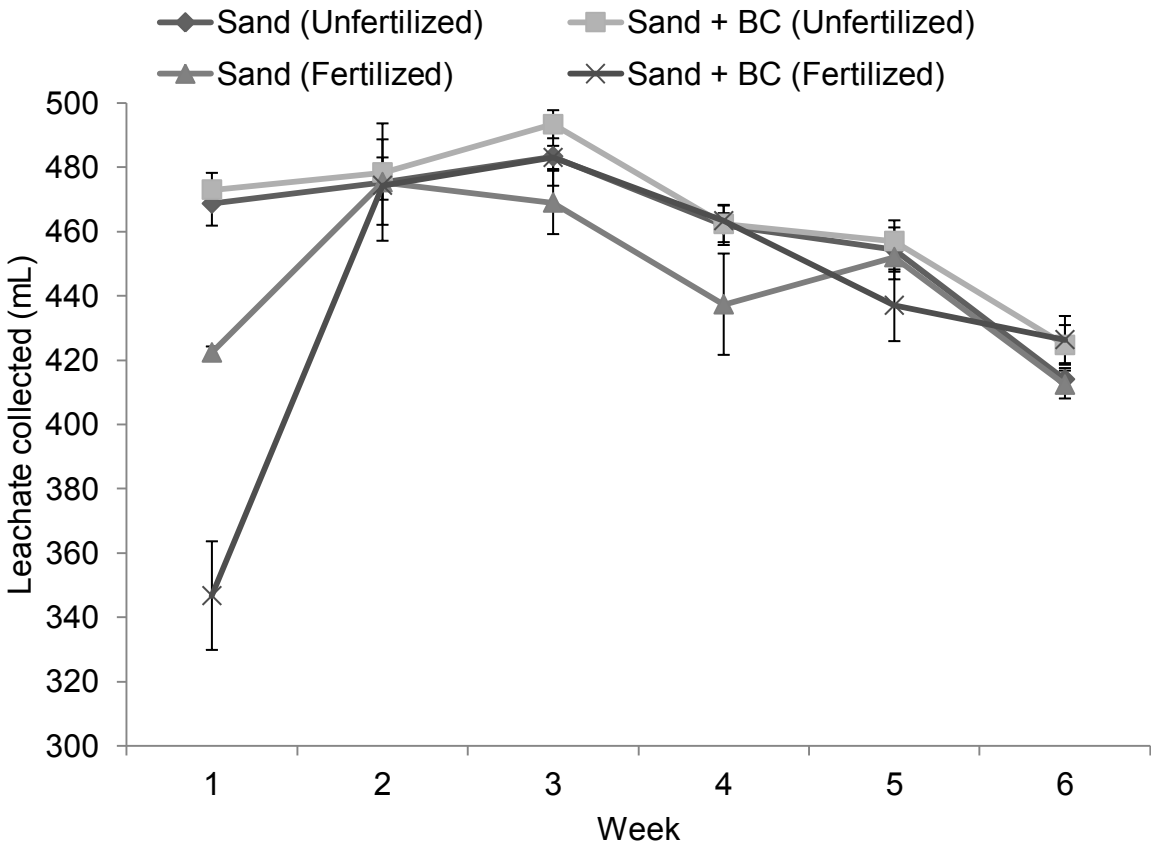


Figure 2.7 Average weekly volumes (mL) of leachates collected over the six week duration of the multi-element leaching study. Each column was leached 520 mL distilled water each week. The individual treatment volumes for each replicate treatment were significant at the P <0.05 level based on the two factorial analysis of variance (ANOVA) with replication.

Table 2.4 Average percent of multi-element fertilizer leachates collected of the total amount of water applied per treatment over six weeks.

	% Water leached of total water applied per week					
	1	2	3	4	5	6
Sand (Unfertilized)	90	91	93	89	87	80
Sand + BC (Unfertilized)	91	92	95	89	88	82
Sand (Fertilized)	81	91	90	84	87	79
Sand + BC (Fertilized)	67	91	93	89	84	82

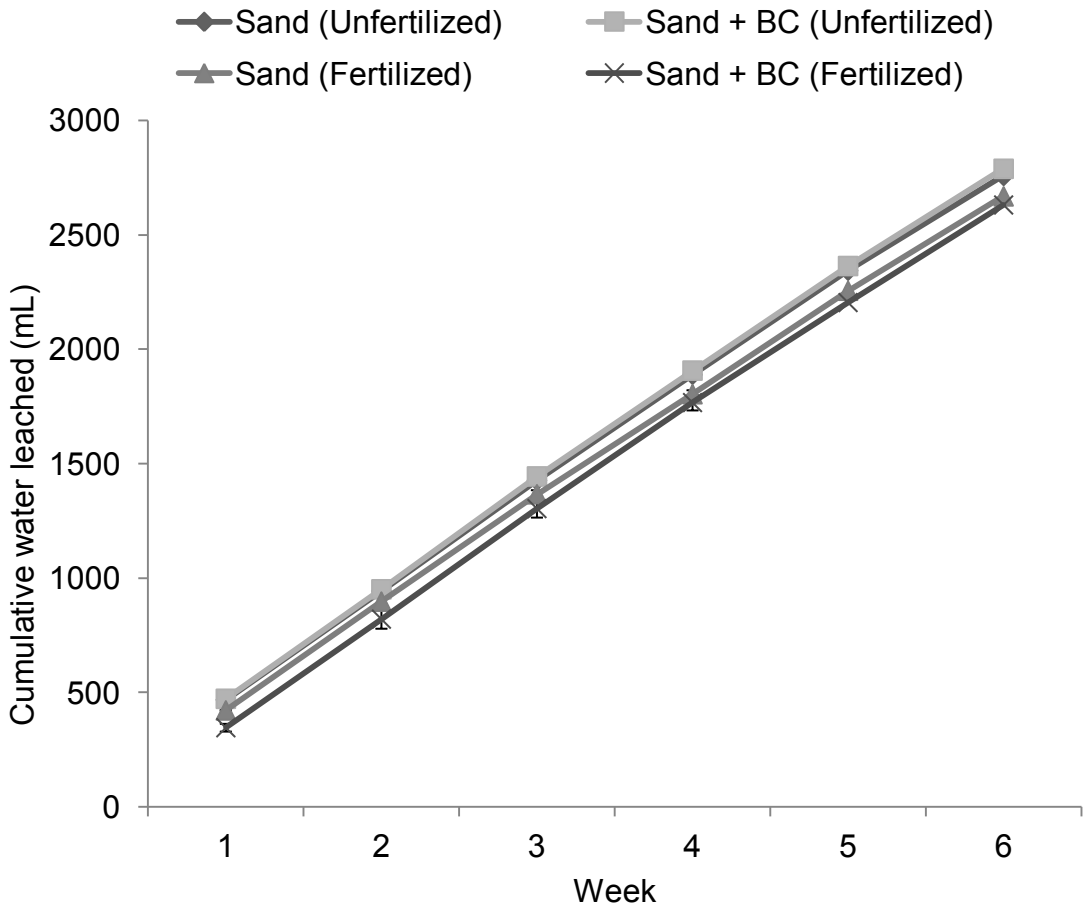


Figure 2.8 Cumulative water leached (mL) over the six week duration of the multi-element leaching study. Each column was leached 520 mL distilled water each week. The individual treatment volumes for each replicate treatment were significant at the $P < 0.05$ level based on the two factorial analysis of variance (ANOVA) without replication.

4.4.3.2 The leachate pH and EC measurements

In the absence of fertilizer, the pH of the leachates collected was acidic in nature during week 1 (Fig. 2.9). The pH of the leachates from the biochar treated soil was 0.37 units lower than the leachates from the control soil, no biochar added. This observation was unexpected as biochar is alkaline in nature and generally increases pH. It is suggested that the distilled water used to leach the soil columns may have caused the lower pH values due to an interaction of the water with atmospheric carbon dioxide.

The leachates collected from the fertilized soil treatments had higher pH values relative to the unfertilized treatments. This is because the multi-element fertilizer raised the leachate pH. During week 1, the pH value of the leachates from the fertilized sand was 6.14; while the leachates from the biochar treated fertilized sand was 6.40. The higher pH from the biochar treated soil is attributed to biochar's alkaline nature.

Reduction reactions are suggested to explain the increase in the pH of leachates during the first two weeks of leaching. During week 3 and 5, the leachate pH remained relatively unchanged for across all treatments. The pH of the leachates collected during week 6 slightly decreased across all treatments.

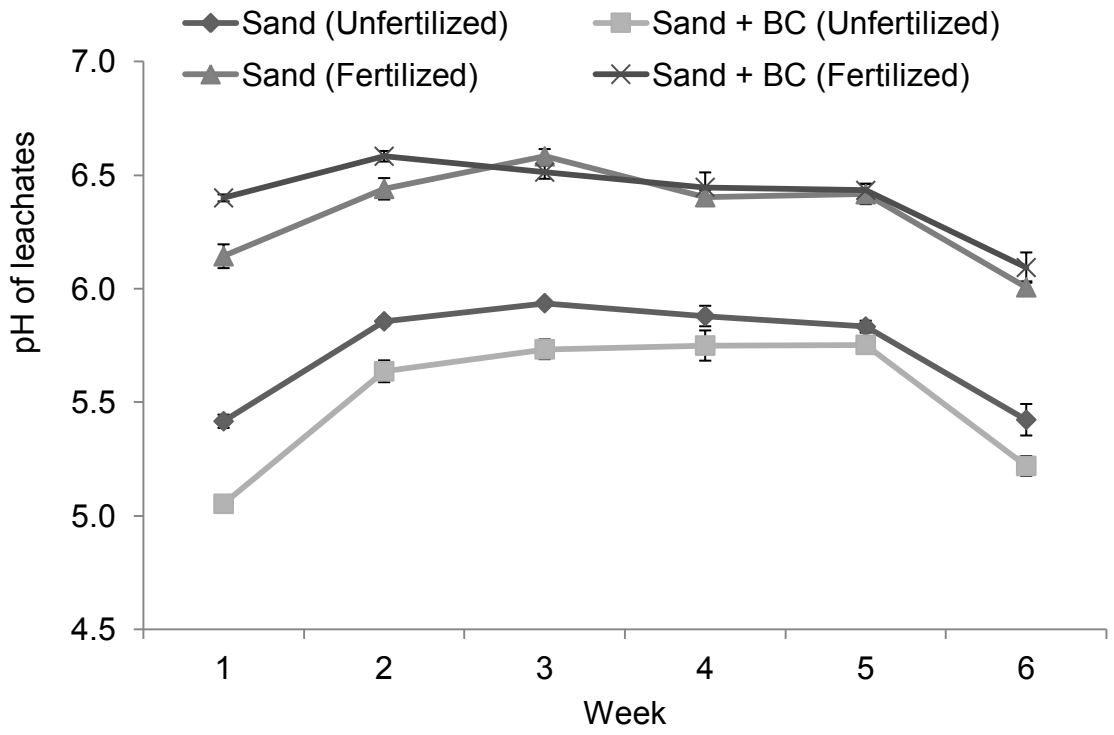


Figure 2.9 The multi-element study weekly leachate pH measurements collected. The individual pH values for each replicate treatment were significant at the P <0.05 level based on the two factorial analysis of variance (ANOVA) with replication.

A sharp, significant reduction in soluble salts of the leachates collected was observed between weeks 1 and 2 for all treatments (Fig. 2.10). This observation correlates with N fertilizer breakthrough curves. From the week 3 onwards, the EC values remained relatively unchanged until the end of the 6 week study. These results were similar to a study conducted by Ding et al. (2010) that showed reduced EC in the leachate of soil columns comprising 0.5 % biochar together with N applied in the form of ammonium chloride.

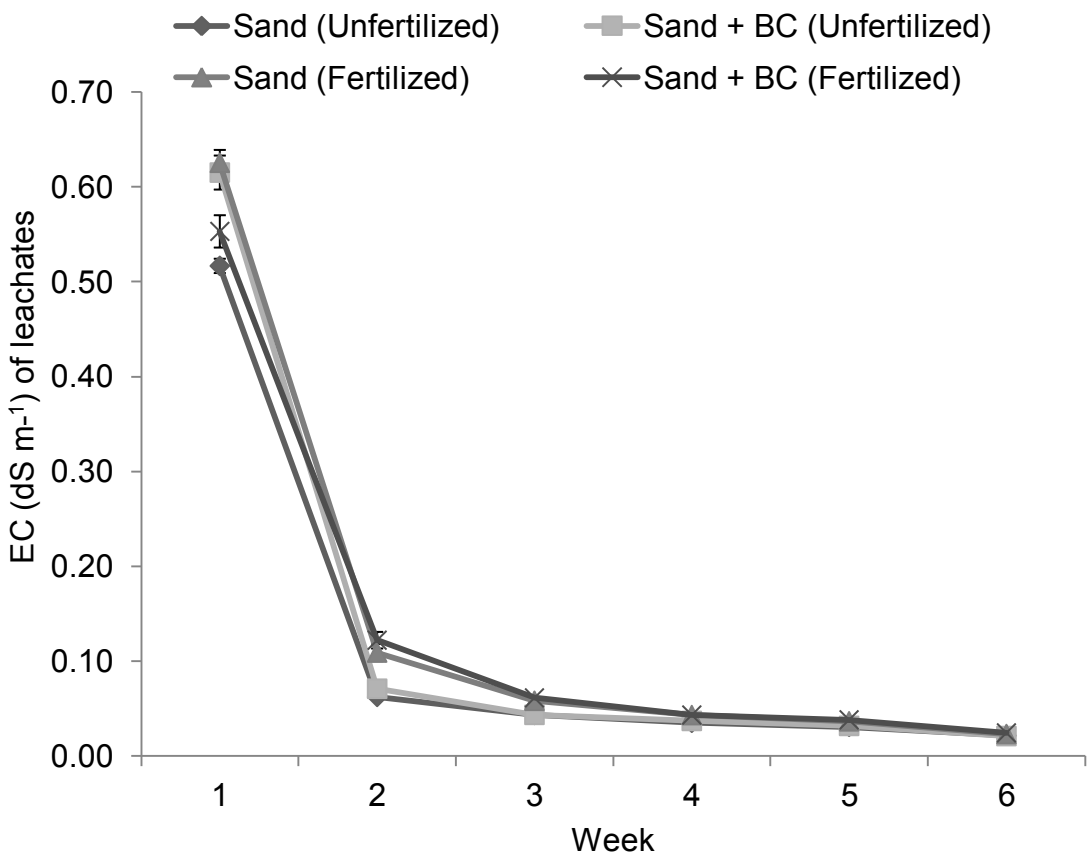


Figure 2.10 Electrical conductivity in the leachate of the multi-element fertilizer leaching study carried out over six weeks.

4.4.3.3 Cumulative multi-element leaching

Figure 2.11 shows that K leaching was reduced in treatments amended with biochar relative to treatments without biochar. The reason why biochar reduces K leaching is likely attributed to its liming potential. The reduction in exchangeable acidity (Chapter 3, Table 1.5) reduces competition with K ions (K^+), thus allowing K to compete with Ca ions (Ca^{2+}) for available exchange sites, and thus reducing K losses due to more K being adsorbed to cation exchange capacity (CEC) (Havlin et al. 2005).

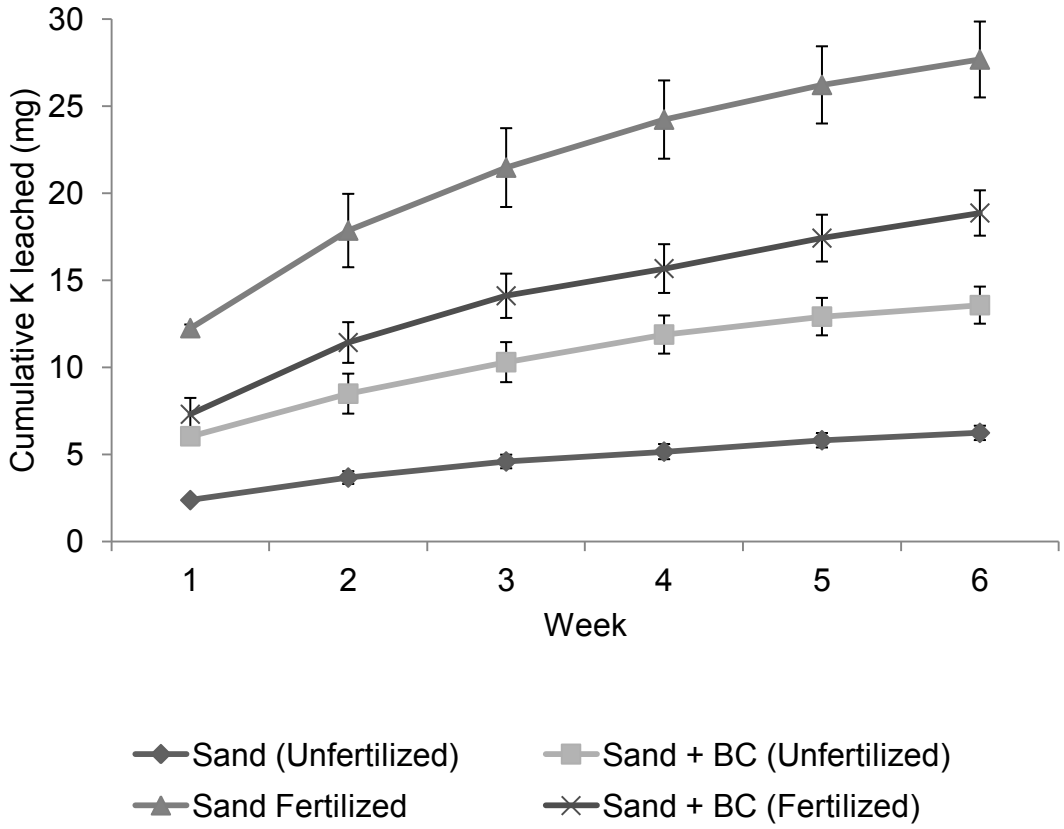


Figure 2.11 Cumulative leaching losses of potassium from the four multi-element nutrient study treatment levels. Namely, sandy soil, without biochar (fertilized and unfertilized), and sandy soil amended with 0.5 % biochar (w/w) (fertilized and unfertilized).

A key finding that this study was aimed at determining was to quantify the amount by which biochar was able to reduce fertilizer leaching. Table 2.5 shows empirical evidence for the ability of biochar to reduce nutrient leaching. Since the soil used for this study has poor buffering capacity, and thus relatively fewer nutrients, the fertilizer leached from the unamended soil was smaller for all the elements, and comparatively much less for K and P. Therefore, as expected, fertilization and the addition of biochar increased and improved the buffer capacity of the sand.

The soil in each column contained 23 mg of water soluble K and the mixture of soil and 0.5 % biochar had 41 mg of extractable K (Chapter 3, Table 1.6). In the absence of fertilizer, the cumulated K losses from the sand and sand-biochar treatments were determined as being about 6 and 14 mg respectively (Table 2.5). In the fertilized sand treatments, less K leached from the biochar-amended soil than the control. Since less fertilizer leached from the biochar-amended sand than from the control

sand, it is suggested that biochar is able to retain K and thus reduce K leaching from sand. Since the fertilizer used was broad spectrum, it added nutrients to the soil solution, and thus simultaneously accelerated the leaching and caused the precipitation of some elements. This is possibly the reason why 118 % of K leached from the unfertilized treatments, while the fertilized columns experienced an overall 31.9 % reduction in K leaching.

Although no water soluble phosphates were detected in the control soil, the 0.5 % biochar-amended soil contained about 2.3 mg P (Chapter 3, Table 1.6). As a result thereof, a very small amount of 0.68 mg was leached from the control soil (Table 2.5). Almost twice the amount of P was leached from the fertilized soil without biochar relative to the fertilized soil with biochar (Table 2.5). This may indicate that the application of biochar to sandy soil retains P. The introduction of P from fertilizer into the biochar-amended soil may have caused an increase in adsorbed $H_2PO_4^-$ while some $H_2PO_4^-$ precipitated as solid P compounds that further added to the buffer capacity of P in soils. It is also suggested that the P added to the soil from the fertilizer may have undergone either P fixation or retention reactions, whereby the P could have either been surface adsorbed by biochar, or alternatively precipitated as secondary P compounds (Havlin et al. 2005).

Biochar reduced Na leaching from the soil columns receiving fertilizer by 19.0 %. Since Na is a competitor with Ca on soil surface sites because of its cationic state, Na is usually lost more readily to leaching (Havlin et al. 2005). Furthermore, since less fertilizer leached from the biochar treated sand than from the control, it is suggested that biochar is able to retain Ca.

Table 2.5 Cumulative mass of elements leached over six weeks in the multi-element leaching study experimental columns and the percent amount that biochar reduced fertilizer leaching.

	Macro-elements (mg)					Micro-elements (mg)		
	K	P	Ca	Mg	Na	Fe	Mn	Zn
Sand (Unfertilized)	6.23	0.68	11.28	5.59	30.76	3.22	0.08	0.15
Sand + BC (Unfertilized)	13.57	2.00	12.65	6.78	31.99	3.44	0.10	0.15
Sand (Fertilized)	27.68	1.43	8.20	4.87	43.26	4.00	0.04	0.11
Sand + BC (Fertilized)	18.87	0.78	5.95	3.14	35.05	3.91	0.03	0.08
Fertilizer leached from sand (mg)	21.45	0.74	-3.09	-0.72	12.50	0.79	-0.044	-0.03
Fertilizer leached from biochar-amended sand (mg)	7.34	1.32	1.37	1.19	1.24	0.219	0.019	0.00
Increase in elements leached (Unfertilized) (%)	117.8	193.7	12.1	-12.8	40.6	24.5	-53.8	-21.6
Reduction in leaching (Fertilized) (%)	31.9	45.3	27.4	35.5	19.0	2.4	16.8	31.0

Magnesium is highly mobile (Taiz and Zeiger 2002) and thus highly susceptible to leaching in sandy soils, particularly following K fertilization. The problem of great amounts of Mg loss in percolating waters is further heightened by its inherent property of being mostly found as exchangeable and in solution (Havlin et al. 2005). Biochar application to sandy soils can be used to address these problems as a 35.5 % reduction in Mg leaching was observed in soil columns receiving fertilizer.

The micro-elements Fe, Mn and Zn showed dissimilar trends concerning the influence of biochar and fertilizer in reducing the amounts of nutrient leaching. In particular, the percent Fe leached from the unfertilized treatments was 24 % and this was exclusively influenced by the addition of biochar since no fertilizer was added. However, the percent Fe reduction in leaching due to biochar and fertilizer was smaller (2.4 %). This was possibly influenced by the ability of Fe to form complexes, especially when organic compounds are added to the soil (Havlin et al. 2005). Furthermore, Mn and Zn leaching was reduced due to the biochar added by 16.8 and 31.0 % respectively.

The results show that lesser quantities of elements were leached out in columns with a combination of biochar and fertilizer. This suggests that the reduction in leaching is a consequence of the addition of biochar. Therefore, for a fundamental basis in understanding nutrient mobility, it is important for electrical neutrality of the soil solution system to be regulated. This needs to be effected by ensuring that anion mobility is simultaneously accompanied by cations mobility (Major et al. 2005).

4.5 Conclusions

The results from the current study demonstrate that biochar can significantly reduce the leaching of highly mobile nutrients such as ammonium, nitrate, and basic cations. Biochar significantly reduced the leaching of ammonium by 12, 50, and 86 % and nitrate by 26, 42, and 95 %, respectively at the 0.5, 2.5, and 10.0 % (w/w) biochar-amended soils relative to the control, no biochar added. Therefore, the results provide evidence that biochar is able to reduce total N leaching over time with the application of increasing levels of biochar.

The 2 M KCl extraction was effective for determining potentially plant available inorganic N remaining in the soil at the completion of the leaching study investigating the application of ammonium nitrate fertilizer. In addition, this extraction allowed us to hypothesise the possible fates of the inorganic N at the end of the six week study. The control soil could contribute up to 1.3 % NH_4-N and 13.8 % NO_3-N as plant available, all of the NH_4-N was leached and only 63.4 % NO_3-N was leached. It is suggested that the additional NH_4-N leached from the control (70.2 %) and 0.5 % treatment (49.2 %) was leached from the inherent soil organic matter. The 0.5 % treatment showed that from all possibly remaining plant available N, none was attributed to NH_4-N and 14.9 % was in the form of NO_3-N, the total N leached was 63.4 % in the form of NO_3-N and 21.7 % NO_3-N may have either been fixed or volatilized. The 2.5 % treatment could contribute up to 11.9 % NH_4-N and 20.5 % NO_3-N as plant available. Also, 85.6 % NH_4-N and 50 % NO_3-N was leached. It was estimated that 2.4 % NH_4-N and 29.5 % NO_3-N was fixed or volatilized. At the highest level of biochar application of 10.0 % (w/w), 64.6 % NH_4-N and 16.9 % NO_3-N was potentially plant available. Since less NO_3-N was extracted as potentially available relative to NH_4-N in the 10.0 % biochar-amended soils, it is suggested that denitrification took place due to the wetness of the leaching columns. Alternatively, temporary N immobilization may have occurred. In addition, biochar significantly reduced N leaching as only 23.1 % NH_4-N and 3.7 % NO_3-N was leached. Lastly, the fixed or volatized fraction attributed to the 10.0 % treatment was 12.3 % from NH_4-N and 79.4 % from NO_3-N.

Biochar (0.5 % application level) reduced the leaching of basic cations, P and micronutrients from the multi-element fertilizer applied. In particular, the fertilized biochar-amended soil treatments showed a reduction in leaching of K (31.9 %), Ca (27.4 %), Mg (35.5 %) and P (45.3 %). In addition, micronutrients in the fertilized biochar-amended soil treatments showed a reduction in leaching of Fe (2.4 %), Mn (16.8 %), and Zn (31.0 %).

Biochar has shown to be highly beneficial in acting as an ion adsorbent as it can greatly reduce the leaching of highly mobile nutrients from fertilizers in sandy soils. This can be effective in keeping it in the rooting zone, and therefore improving its efficacy or providing a better opportunity for crops to absorb N and basic cations. In addition, it is suggested that biochar can be used by adding it below the rooting zone to prevent or reduce inorganic fertilizers from contaminating surface and groundwaters. It could also be used as a protective layer in the soil below pit toilets or polluted sites to retard nutrients from entering groundwater.

Future research should include investigating the effects of biochar amendment on sandy loam and clay soils. In addition, research should be conducted on long-term field experiments that specifically focus on the transport and mobility of biochar in the agricultural landscape. Such research will be critical in understanding biochar's patterns of redistribution and accumulation, thus providing information on the long-term effect of biochar on soil properties.

CHAPTER 5

5 General Discussion and Conclusions

The aim of this research was to investigate the effect of the interaction of locally produced biochar (charcoal) applied to acidic, sandy Western Cape soil on their chemistry, nutrient uptake and fertilizer mobility. Biochar has been described as the solid product material produced during pyrolysis for use as a soil amendment, applied with the intention of increasing the agronomic productivity of soils.

In Chapter 3, a thorough chemical laboratory analysis of the sandy soil mixed with four biochar application levels (0.05, 0.5, 2.5, and 10.0 % w/w), and a control (no biochar added) was performed. It was found that the addition of biochar led to a significant increase in soil pH, exchangeable basic cations, potentially plant available P, and water holding capacity. The immediate increase in soil pH observed at increasing biochar application levels was attributed to biochar's alkalinity content. This suggests that caution should be taken when applying biochar to sandy soil as raising the pH over 6.50 (in water) results in over-liming and micronutrient deficiencies (Zn, Cu, and B).

The wheat pot trial showed that the optimum biochar application level based on the above ground biomass production was 0.5 % (w/w) (approximately 10 t ha^{-1} to a depth of 15 cm) for fertilized wheat grown for i) 12 weeks (21 % biomass increase) and ii) to maturity (15 % biomass increase). It is suggested that the 0.5 % (w/w) biochar application level experienced maximum plant growth due to increased K uptake. In addition, because the 0.5 % level had a fairly neutral soil pH of 6.80 (in water) before planting, no micronutrient deficiencies were experienced, which could have been prompted by a high soil pH. The unfertilized wheat treatments grown for 12 weeks showed an optimum biochar application level of 2.5 % (w/w) (approximately 50 t ha^{-1} to a depth of 15 cm), and showed a 29 % biomass increase. It is suggested that the high Mn uptake efficiency at the 2.5 % level was the key reason for optimum biomass production in the absence of fertilizer. Furthermore, because biochar reduced exchangeable acidity, increased soil pH of the acid soil, inherently contains significant amounts of plant nutrients such as K, Ca and Mg, and improved the water holding capacity of the sandy soil; it kept the soil wetter for

longer due to its microporous nature, and therefore provided the main reasons for enhanced plant growth.

In contrast some of the negative plant growth responses observed showed that increasing biochar application levels increased the C:N ratio of the soil and appeared to reduce N uptake possibly because of N immobilization. This might only be a temporary effect because following the breakdown of the more labile, volatile C component of the biochar, immobilization is expected to be reduced. Negative growth responses relative to the controls were observed at the 10.0 % levels for the wheat grown for 12 weeks with reductions of above ground biomass of 89 % and 293 % for the unfertilized and fertilized treatments respectively. The fertilized wheat pot trial treatments grown to maturity showed a 13 % decrease in above ground biomass production in comparison to the control. The inhibited wheat growth was attributed to a combination of over-limed and wetter soil conditions, accompanied by nutrient deficiencies of N, P, Zn, B, Mn and Cu.

In Chapter 4 the effect of biochar on fertilizer mobility in sandy soil was investigated on the same soil and biochar used in Chapter 3. The results from the first experiment of the study found that biochar can significantly reduce leaching of the inorganic N fertilizer ammonium nitrate over six weeks. Sandy soil amended with biochar applied at 0.5, 2.5, and 10.0 % (w/w) significantly reduced the leaching of ammonium by 12, 50, and 86 % and nitrate by 26, 42, and 95 %, respectively, relative to the control, no biochar added. Therefore, biochar can reduce total N leaching over time with the application of increasing levels of biochar.

At the completion of the N leaching study, potentially plant available inorganic N remaining in the soil was determined using a 2 M KCl extraction. It was hypothesised that the fate of the inorganic N forms (NH_4 and NO_3) could be determined as being either i) potentially plant available, as determined by the 2 M KCl extraction, ii) leached and iii) fixed or volatilized. Biochar applied to sandy soil effectively increased the potentially plant available NO_3-N by 13.8 % (control), 14.9 % (0.5 % treatment), 20.5 % (2.5 % treatment) and 16.9 % (10.0 %). Biochar significantly reduced NH_4-N and NO_3-N leaching over time. Ammonium nitrogen leaching was reduced from total NH_4-N leached at the control to 23.1 % leached at the 10.0 % biochar treatment. Nitrate nitrogen leaching was reduced from 85.4 % at the control to 3.7 % leached at

the 10.0 % biochar treatment. In addition, increasing biochar treatments increased the amount of fixed or volatilized NO_3-N from 0.5 % (21.7 %), 2.5 % (29.5 %) and 10.0 % (79.4 %).

The results from the multi-element leaching study found that biochar (0.5 % application level) can significantly reduce the leaching of highly mobile basic cations, P and micronutrients, In particular, the fertilized biochar-amended soil treatments showed a reduction in leaching of K (31.9 %), Ca (27.4 %), Mg (35.5 %) and P (45.3 %). The micronutrients in the fertilized biochar-amended soil treatments showed a reduction in leaching of Fe (2.4 %), Zn (31.0 %) and Mn (16.8 %).

Therefore, the results from this study highlight that there are several benefits to biochar amendment, especially on sandy soils where the prevention of nutrient leaching is one of the best reasons.

5.1 Recommendations and Future Research

The exclusive use of biochar in the absence of N fertilizer is not encouraged because as the results from this study show, a high C:N ratio of soil caused by increasing biochar application levels suppresses N uptake to the growing plant. This is possibly due to temporary N immobilization, and thereby results in N deficiencies. Also, since the study showed that micronutrient deficiencies resulted due to increased soil pH, supplementary micronutrients are recommended with fertilizer application to combat deficiencies. Overall, based on the improved soil nutrient status and maximum plant growth results, it is recommended that biochar not be applied on acidic, sandy soils at levels greater than 0.5 % biochar (w/w), approximately 10 t ha^{-1} at 15 cm depth.

This study has shown that because biochar is an effective ion adsorbent, it can greatly reduce the leaching of highly mobile nutrients from fertilizers in sandy soils. This will allow nutrients to be kept in the rooting zone, and therefore improve the efficiency of fertilizers. Further, adding biochar to below the rooting zone of plants can aid in preventing or reducing the contamination of surface and groundwaters by inorganic fertilizers. Biochar also warrants merit in using it as a protective layer in the soil below pit toilets or polluted sites with the aim of retarding nutrients from seeping into groundwater.

In view of the positive and negative plant growth responses obtained in this study, a long-term field trial of biochar application to soils is a highly pertinent area for future research. Such research should investigate the amendment of soils of different textures with biochar. This would better contribute to scientific knowledge on making sound recommendations on the use of biochar in a range of agricultural soils. Also, because biochar properties such as pH and nutrient availability are dependent on the feedstock and pyrolysis conditions under which biochar is produced, it is recommended that various pyrolysis processes are investigated on a variety of feedstocks aimed at producing biochar for soil application. Since the use of slow release fertilizers and the efficiency of organic N fertilizers in biochar-amended soils are sparsely assessed, its implications must be fully explored. Further, the fate of biochar in the agricultural landscape needs to be investigated with a focus on its transport and mobility.

Research on the application of biochar as a soil amendment in South Africa is relatively new and therefore further research is necessary to build a strong scientific database and knowledge. This would greatly contribute to scientific literature in facilitating a clearer understanding of the changes in nutrient availability and alkalinity in soil over time as a result of addition of biochar to agricultural soils. Clearly, this highlights the importance of future research to establish the long-term effect of biochar application on soil.

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